



US008461071B2

(12) **United States Patent**  
**D'Evelyn**

(10) **Patent No.:** **US 8,461,071 B2**  
(45) **Date of Patent:** **Jun. 11, 2013**

(54) **POLYCRYSTALLINE GROUP III METAL  
NITRIDE WITH GETTER AND METHOD OF  
MAKING**

(75) Inventor: **Mark P. D'Evelyn**, Goleta, CA (US)

(73) Assignee: **Soraa, Inc.**, Fremont, CA (US)

(\*) Notice: Subject to any disclaimer, the term of this  
patent is extended or adjusted under 35  
U.S.C. 154(b) by 379 days.

(21) Appl. No.: **12/634,665**

(22) Filed: **Dec. 9, 2009**

(65) **Prior Publication Data**

US 2010/0151194 A1 Jun. 17, 2010

**Related U.S. Application Data**

(60) Provisional application No. 61/122,332, filed on Dec.  
12, 2008.

(51) **Int. Cl.**  
**C04B 35/00** (2006.01)  
**C01B 21/06** (2006.01)

(52) **U.S. Cl.**  
USPC ..... **501/96.1**; 501/96.2; 423/409

(58) **Field of Classification Search**  
USPC ..... 501/96.1, 96.2, 96.4, 97.1, 97.2,  
501/97.3, 98.4, 98.5; 423/409  
See application file for complete search history.

(56) **References Cited**

**U.S. PATENT DOCUMENTS**

3,245,760 A 4/1966 Sawyer  
3,303,053 A 2/1967 Strong et al.  
3,335,084 A 8/1967 Hall

4,030,966 A 6/1977 Hornig et al.  
4,430,051 A 2/1984 Von Platen  
5,868,837 A 2/1999 DiSalvo et al.  
6,090,202 A 7/2000 Klipov  
6,129,900 A 10/2000 Satoh et al.  
6,152,977 A 11/2000 D'Evelyn  
6,350,191 B1 2/2002 D'Evelyn et al.  
6,372,002 B1 4/2002 D'Evelyn et al.  
6,398,867 B1 6/2002 D'Evelyn et al.  
6,406,776 B1 6/2002 D'Evelyn  
6,455,877 B1 9/2002 Ogawa et al.  
6,475,254 B1 11/2002 Saak et al.  
6,533,874 B1 3/2003 Vaudo et al.  
6,541,115 B2 4/2003 Pender et al.

(Continued)

**FOREIGN PATENT DOCUMENTS**

JP 2005-289797 A2 10/2005  
JP 2007-039321 A 2/2007

(Continued)

**OTHER PUBLICATIONS**

International Search Report and Written Opinion of PCT Application  
No. PCT/US09/67745, dated Feb. 5, 2010, 14 pages total.

(Continued)

*Primary Examiner* — Kaj K Olsen

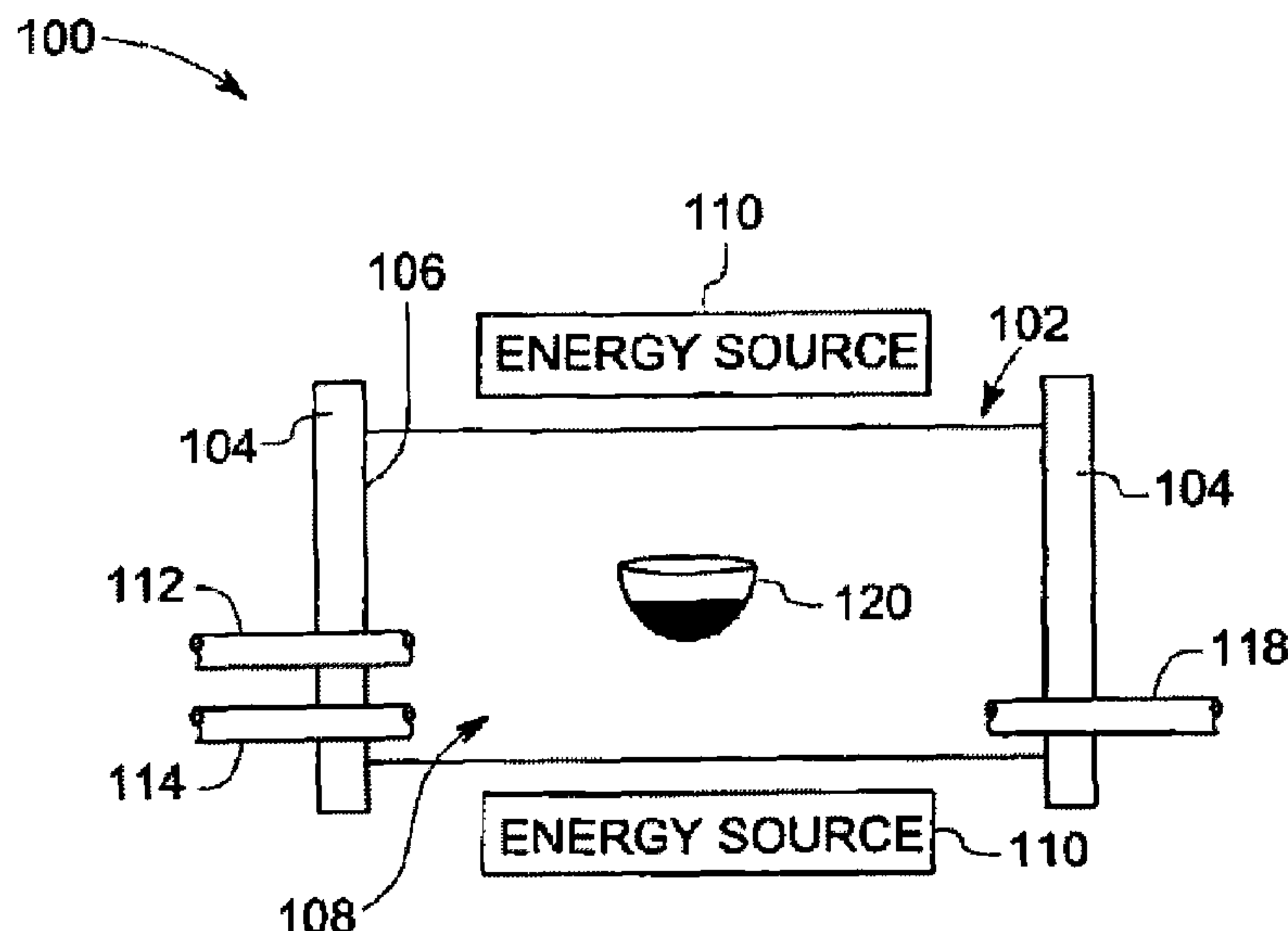
*Assistant Examiner* — Noah Wiese

(74) *Attorney, Agent, or Firm* — Kilpatrick Townsend &  
Stockton LLP

(57) **ABSTRACT**

A gettered polycrystalline group III metal nitride is formed by heating a group III metal with an added getter in a nitrogen-containing gas. Most of the residual oxygen in the gettered polycrystalline nitride is chemically bound by the getter. The gettered polycrystalline group III metal nitride is useful as a raw material for ammonothermal growth of bulk group III nitride crystals.

**18 Claims, 5 Drawing Sheets**



U.S. PATENT DOCUMENTS							
6,596,040	B2	7/2003	Saak et al.	2003/0164507	A1	9/2003	Edmond et al.
6,596,079	B1	7/2003	Vaudo et al.	2003/0183155	A1	10/2003	D'Evelyn et al.
6,639,925	B2	10/2003	Niwa et al.	2003/0209191	A1	11/2003	Purdy
6,656,615	B2	12/2003	Dwilinski et al.	2003/0232512	A1	12/2003	Dickinson et al.
6,764,297	B2	7/2004	Godwin et al.	2004/0000266	A1	1/2004	D'Evelyn et al.
6,765,240	B2	7/2004	Tischler et al.	2004/0023427	A1	2/2004	Chua et al.
6,784,463	B2	8/2004	Camras et al.	2004/0104391	A1	6/2004	Maeda et al.
6,787,814	B2	9/2004	Udagawa	2004/0124435	A1	7/2004	D'Evelyn et al.
6,806,508	B2	10/2004	D'Evelyn et al.	2004/0161222	A1	8/2004	Niida et al.
6,858,882	B2	2/2005	Tsuda et al.	2004/0222357	A1	11/2004	King et al.
6,861,130	B2	3/2005	D'Evelyn et al.	2005/0087753	A1	4/2005	D'Evelyn et al.
6,936,488	B2	8/2005	D'Evelyn et al.	2005/0098095	A1	5/2005	D'Evelyn et al.
6,955,719	B2	10/2005	Dmitriev et al.	2005/0109240	A1	5/2005	Maeta et al.
7,001,577	B2 *	2/2006	Zimmerman et al. .... 423/290	2005/0121679	A1	6/2005	Nagahama et al.
7,009,215	B2	3/2006	D'Evelyn et al.	2005/0128469	A1	6/2005	Hall et al.
7,012,279	B2	3/2006	Wierer, Jr. et al.	2005/0152820	A1	7/2005	D'Evelyn et al.
7,026,755	B2	4/2006	Setlur et al.	2005/0167680	A1	8/2005	Shei et al.
7,033,858	B2	4/2006	Chai et al.	2005/0191773	A1	9/2005	Suzuki et al.
7,053,413	B2	5/2006	D'Evelyn et al.	2005/0205215	A1	9/2005	Giddings et al.
7,063,741	B2	6/2006	D'Evelyn et al.	2005/0263791	A1	12/2005	Yanagihara et al.
7,067,407	B2	6/2006	Kostamo et al.	2006/0030738	A1	2/2006	Vanmaele et al.
7,078,731	B2	7/2006	D'Evelyn et al.	2006/0032428	A1	2/2006	Dwilinski et al.
7,098,487	B2	8/2006	D'Evelyn et al.	2006/0037529	A1	2/2006	D'Evelyn et al.
7,101,433	B2	9/2006	D'Evelyn et al.	2006/0037530	A1	2/2006	Dwilinski et al.
7,102,158	B2	9/2006	Tysoe et al.	2006/0038193	A1	2/2006	Wu et al.
7,105,865	B2	9/2006	Nakahata et al.	2006/0048699	A1	3/2006	D'Evelyn et al.
7,112,829	B2	9/2006	Picard et al.	2006/0096521	A1	5/2006	D'Evelyn et al.
7,119,372	B2	10/2006	Stokes et al.	2006/0118799	A1	6/2006	D'Evelyn et al.
7,122,827	B2	10/2006	Alizadeh et al.	2006/0163589	A1	7/2006	Fan et al.
7,125,453	B2	10/2006	D'Evelyn et al.	2006/0169993	A1	8/2006	Fan et al.
7,160,388	B2	1/2007	Dwilinski et al.	2006/0177362	A1	8/2006	D'Evelyn et al.
7,160,531	B1	1/2007	Jacques et al.	2006/0207497	A1	8/2006	D'Evelyn et al.
7,175,704	B2	2/2007	D'Evelyn et al.	2006/0213429	A1	9/2006	D'Evelyn et al.
7,198,671	B2	4/2007	Ueda	2006/0214287	A1	9/2006	Motoki et al.
7,208,393	B2	4/2007	Haskell et al.	2006/0228870	A1	9/2006	Ogihara et al.
7,220,658	B2	5/2007	Haskell et al.	2006/0246687	A1	10/2006	Oshima
7,252,712	B2	8/2007	Dwilinski et al.	2006/0246687	A1	11/2006	Kaiser et al.
7,285,801	B2	10/2007	Eliashevich et al.	2006/0255343	A1	11/2006	Kaiser et al.
7,291,544	B2	11/2007	D'Evelyn et al.	2006/0289386	A1	11/2006	Ogihara et al.
7,316,746	B2	1/2008	D'Evelyn et al.	2007/0015345	A1	12/2006	Tysoe et al.
7,329,371	B2	2/2008	Setlur et al.	2007/0057337	A1	1/2007	Baker et al.
7,335,262	B2	2/2008	Dwilinski et al.	2007/0057337	A1	3/2007	Kano et al.
7,338,828	B2	3/2008	Imer et al.	2007/0077674	A1	4/2007	Okuyama et al.
7,358,542	B2	4/2008	Radkov et al.	2007/0096239	A1	5/2007	Cao et al.
7,364,619	B2	4/2008	Dwilinski et al.	2007/0105351	A1	5/2007	Motoki et al.
7,368,015	B2	5/2008	D'Evelyn et al.	2007/0114569	A1	5/2007	Wu et al.
7,381,391	B2	6/2008	Spencer et al.	2007/0121690	A1	5/2007	Wu et al.
7,420,261	B2	9/2008	Dwilinski et al.	2007/0121690	A1	5/2007	Fujii et al.
7,572,425	B2	8/2009	McNulty et al.	2007/0131967	A1	6/2007	Kawaguchi et al.
7,625,446	B2	12/2009	D'Evelyn et al.	2007/0141819	A1 *	6/2007	Park et al. .... 438/584
7,642,122	B2	1/2010	Tysoe et al.	2007/0142204	A1 *	6/2007	Park et al. .... 501/98.4
7,705,276	B2	4/2010	Giddings et al.	2007/0151509	A1	7/2007	Park
7,759,710	B1	7/2010	Chiu et al.	2007/0158785	A1	7/2007	D'Evelyn et al.
7,871,839	B2	1/2011	Lee et al.	2007/0164292	A1	7/2007	Okuyama
7,976,630	B2	7/2011	Poblenz et al.	2007/0166853	A1	7/2007	Guenther et al.
8,021,481	B2	9/2011	D'Evelyn	2007/0178039	A1	7/2007	Guenther et al.
8,048,225	B2	11/2011	Poblenz et al.	2007/0181056	A1	8/2007	D'Evelyn et al.
8,097,081	B2	1/2012	D'Evelyn	2007/0190758	A1	8/2007	D'Evelyn et al.
8,148,801	B2	4/2012	D'Evelyn	2007/0197004	A1	8/2007	Kaeding et al.
8,188,504	B2	5/2012	Lee	2007/0210074	A1	8/2007	Dadgar et al.
8,198,643	B2	6/2012	Lee et al.	2007/0215033	A1	9/2007	Maurer et al.
8,207,548	B2	6/2012	Nagai	2007/0228404	A1	9/2007	Imaeda et al.
8,284,810	B1	10/2012	Sharma et al.	2007/0234946	A1	10/2007	Tran et al.
8,299,473	B1	10/2012	D'Evelyn et al.	2007/0252164	A1	10/2007	Hashimoto et al.
8,303,710	B2	11/2012	D'Evelyn	2007/0274359	A1	11/2007	Zhong et al.
8,306,081	B1	11/2012	Schmidt et al.	2007/0290224	A1	11/2007	Takeuchi et al.
8,323,405	B2	12/2012	D'Evelyn	2008/0006831	A1	12/2007	Ogawa
8,329,511	B2	12/2012	D'Evelyn	2008/0006831	A1	1/2008	Ng
2001/0009134	A1	7/2001	Kim et al.	2008/0008855	A1	1/2008	D'Evelyn et al.
2001/0011935	A1	8/2001	Lee et al.	2008/0023691	A1	1/2008	Jang et al.
2001/0048114	A1	12/2001	Morita et al.	2008/0025360	A1	1/2008	Eichler et al.
2002/0070416	A1	6/2002	Morse et al.	2008/0073660	A1	3/2008	Ohno et al.
2002/0105986	A1	8/2002	Yamasaki	2008/0083741	A1	4/2008	Giddings et al.
2002/0182768	A1	12/2002	Morse et al.	2008/0083929	A1	4/2008	Fan et al.
2002/0189532	A1	12/2002	Motoki et al.	2008/0087919	A1	4/2008	Tysoe et al.
2003/0027014	A1	2/2003	Johnson et al.	2008/0106212	A1	4/2008	Tysoe et al.
2003/0140845	A1	7/2003	D'Evelyn et al.	2008/0121906	A1	5/2008	Yen et al.
2003/0145784	A1	8/2003	Thompson et al.	2008/0128752	A1	5/2008	Yakushiji
				2008/0156254	A1	6/2008	Wu
				2008/0193363	A1	7/2008	Dwilinski et al.
				2008/0198881	A1	8/2008	Tsuji
				2008/0211416	A1	8/2008	Farrell et al.
				2008/0230765	A1	9/2008	Negley et al.
						9/2008	Yoon et al.



2008/0272462 A1 11/2008 Shimamoto  
 2008/0282978 A1 11/2008 Butcher et al.  
 2008/0285609 A1 11/2008 Ohta et al.  
 2008/0298409 A1 12/2008 Yamashita et al.  
 2009/0078955 A1 3/2009 Fan et al.  
 2009/0092536 A1 4/2009 Kawabata et al.  
 2009/0146170 A1 6/2009 Zhong et al.  
 2009/0218593 A1 9/2009 Kamikawa et al.  
 2009/0250686 A1 10/2009 Sato et al.  
 2009/0301387 A1 12/2009 D'Evelyn  
 2009/0301388 A1 12/2009 D'Evelyn  
 2009/0309110 A1 12/2009 Raring et al.  
 2009/0320744 A1 12/2009 D'Evelyn et al.  
 2009/0320745 A1 12/2009 D'Evelyn et al.  
 2010/0001300 A1 1/2010 Raring et al.  
 2010/0003492 A1 1/2010 D'Evelyn  
 2010/0025656 A1 2/2010 Raring et al.  
 2010/0031872 A1 2/2010 D'Evelyn  
 2010/0031873 A1 2/2010 D'Evelyn  
 2010/0031874 A1 2/2010 D'Evelyn  
 2010/0031875 A1 2/2010 D'Evelyn  
 2010/0031876 A1 2/2010 D'Evelyn  
 2010/0032691 A1 2/2010 Kim  
 2010/0108985 A1 5/2010 Chung et al.  
 2010/0109030 A1 5/2010 Krames et al.  
 2010/0117101 A1 5/2010 Kim et al.  
 2010/0117118 A1 5/2010 Dabiran et al.  
 2010/0147210 A1 6/2010 D'Evelyn  
 2010/0151194 A1 6/2010 D'Evelyn  
 2010/0219505 A1 9/2010 D'Evelyn  
 2010/0295088 A1 11/2010 D'Evelyn et al.  
 2011/0017298 A1 1/2011 Lee  
 2011/0100291 A1 5/2011 D'Evelyn  
 2011/0108081 A1 5/2011 Werthen et al.  
 2011/0121331 A1 5/2011 Simonian et al.  
 2011/0175200 A1 7/2011 Yoshida  
 2011/0183498 A1 7/2011 D'Evelyn  
 2011/0220912 A1 9/2011 D'Evelyn  
 2011/0256693 A1 10/2011 D'Evelyn et al.  
 2011/0262773 A1 10/2011 Poblentz et al.  
 2012/0000415 A1 1/2012 D'Evelyn et al.  
 2012/0007102 A1 1/2012 Feezell et al.  
 2012/0073494 A1 3/2012 D'Evelyn  
 2012/0091465 A1 4/2012 Krames et al.  
 2012/0118223 A1 5/2012 D'Evelyn  
 2012/0137966 A1 6/2012 D'Evelyn et al.  
 2012/0187412 A1 7/2012 D'Evelyn et al.  
 2012/0199952 A1 8/2012 D'Evelyn et al.

## FOREIGN PATENT DOCUMENTS

WO WO 2005121415 A1 12/2005  
 WO WO2007/004495 1/2007  
 WO WO2012-016033 2/2012

## OTHER PUBLICATIONS

Callahan et al., "Synthesis and Growth of Gallium Nitride by the Chemical Vapor Reaction Process (CVRP)," 1999, MRS Internet Journal Nitride Semiconductor Research, vol. 4, Issue No. 10, pp. 1-6.  
 D'Evelyn et al., "Bulk GaN Crystal Growth by the High-Pressure Ammonothermal Method," Journal of Crystal Growth, 2007, vol. 300, pp. 11-16.  
 Dwilinski et al., "Excellent Crystallinity of Truly Bulk Ammonothermal GaN," Journal of Crystal Growth, 2008, vol. 310, pp. 3911-3916.  
 Ehrentraut et al., "Prospects for the Ammonothermal Growth of Large GaN Crystal," Journal of Crystal Growth, 2007, vol. 305, pp. 304-310.  
 Oshima et al., "Thermal and Optical Properties of Bulk GaN Crystals Fabricated Through Hydride Vapor Phase Epitaxy with Void-Assisted Separation," 2005, Journal of Applied Physics, vol. 98, pp. 103509-1-103509-3.  
 Wang et al., "Ammonothermal Synthesis of III-Nitride Crystals," Crystal Growth & Design, 2006, vol. 6, Issue No. 6, pp. 1227-1246.  
 Wang et al., "Synthesis of Dense Polycrystalline GaN of High Purity by the Chemical Vapor Reaction Process," Journal of Crystal Growth, 2006, vol. 286, pp. 50-54.

Byrappa et al., "Handbook of Hydrothermal Technology: A Technology for Crystal Growth and Materials Processing," Noyes Publications, Park Ridge, New Jersey, 2001, pp. 94-96 and 152.  
 Dwiliński et al., AMMONO Method of BN, AlN, and GaN Synthesis and Crystal Growth, Journal of Nitride Semiconductor Research, 1998, 3,25, MRS, Internet: <http://nsr.mij.mrs.org>.  
 Farrell et al., "Continuous-wave Operation of AlGaIn-cladding-free Nonpolar m-Plane InGaIn/GaN Laser Diodes," 2007, Japanese Journal of Applied Physics, vol. 46, No. 32, pp. L761-L763.  
 Feezell et al., "AlGaIn-Cladding-Free Nonpolar InGaIn/GaN Laser Diodes," Japanese Journal of Applied Physics, vol. 46, No. 13, pp. L284-L286, 2007.  
 Frayssinet et al., "Evidence of Free Carrier Concentration Gradient Along the c-axis for Undoped GaN Single Crystals," Journal of Crystal Growth, 2001, vol. 230, pp. 442-447.  
 Hashimoto et al., "Ammonothermal growth of bulk GaN," Journal of Crystal Growth 310:3907-3910 (Aug. 2008).  
 Hashimoto et al., "A GaN bulk crystal with improved structural quality grown by the ammonothermal method," Nature Materials 6:568-671 (Jul. 2007).  
 Iso et al., "High Brightness Blue InGaIn/GaN Light Emitting Diode on Nonpolar m-plane Bulk GaN Substrate," 2007, Japanese Journal of Applied Physics, vol. 46, No. 40, pp. L960-L962.  
 Kim et al., "Improved Electroluminescence on Nonpolar m-plane InGaIn/GaN Quantum Well LEDs," 2007, Physica Status Solidi (RRL), vol. 1, No. 3, pp. 125-127.  
 Kojima et al., "Stimulated Emission at 474 nm from an InGaIn Laser Diode Structure Grown on a (1122) GaN Substrate," 2007, Applied Physics Letter, vol. 91, No. 25, pp. 251107-251107-3.  
 Kolis et al., "Crystal Growth of Gallium Nitride in Supercritical Ammonia," Journal of Crystal Growth, 2001, vol. 222, pp. 431-434.  
 Kolis et al., "Materials Chemistry and Bulk Crystal Growth of Group III Nitrides in Supercritical Ammonia" Mat. Res. Soc. Symp. Proc., 1998, vol. 495, pp. 367-372.  
 Kubota et al., "Temperature Dependence of Polarized Photoluminescence from Nonpolar m-plane InGaIn Multiple Quantum Wells for Blue Laser Diodes" 2008, Applied Physics Letter, vol. 92, pp. 011920-011920-3.  
 Mirwald et al., "Low-Friction Cell for Piston-Cylinder High Pressure Apparatus," Journal of Geophysical Research, 1975, vol. 80, No. 11, pp. 1519-1525.  
 Motoki et al., "Growth and Characterization of Freestanding GaN Substrates," Journal of Crystal Growth, 2002, vol. 237-239, pp. 912-921.  
 Murota et al., "Solid State Light Source Fabricated with YAG:Ce Single Crystal," 2002, Japanese Journal of Applied Physics, vol. 46, No. 41, Part 2, No. 8A, pp. L887-L888.  
 Okamoto et al., "Continuous-Wave Operation of m-Plane InGaIn Multiple Quantum Well Laser Diodes," 2007, Japanese Journal of Applied Physics, vol. 46, No. 9, pp. L187-L189.  
 Okamoto et al., "Pure Blue Laser Diodes Based on Nonpolar m-Plane Gallium Nitride with InGaIn Waveguiding Layers," 2007, Japanese Journal of Applied Physics, vol. 46, No. 35, pp. L820-L822.  
 Peters, "Ammonothermal Synthesis of Aluminium Nitride," Journal of Crystal Growth, 1999, vol. 4, pp. 411-418.  
 Sarva, et al., "Dynamic compressive strength of silicon carbide under uniaxial compression," Mat. Sci. & Eng. A 317,140 (2001).  
 Sato et al., "High Power and High Efficiency Green Light Emitting Diode on free-Standing Semipolar (1122) Bulk GaN Substrate," 2007, Physica Status Solidi (RRL), vol. 1, pp. 162-164.  
 Sato et al., "Optical Properties of Yellow Light-Emitting-Diodes Grown on Semipolar (1122) Bulk GaN Substrate," 2008, Applied Physics Letter, vol. 92, No. 22, pp. 221110-1-221110-3.  
 Schmidt et al., "Demonstration of Nonpolar m-Plane InGaIn/GaN Laser Diodes," 2007, Japanese Journal of Applied Physics, vol. 46, No. 9, L190-L191.  
 Sizov et al., "500-nm Optical Gain Anisotropy of Semipolar (1122) InGaIn Quantum Wells," 2009, Applied Physics Express, vol. 2, pp. 071001-1-071001-3.  
 Tsuda et al., "Blue Laser Diodes Fabricated on m-Plane GaN Substrates," 2008, Applied Physics Express, vol. 1, pp. 011104-011104-03.



- Tyagi et al., "Semipolar (1011) InGaN/GaN Laser Diodes on Bulk GaN Substrates," 2007, Japanese Journal of Applied Physics, vol. 46, No. 19, pp. L444-L445.
- Wang et al., "Ammonothermal growth of GaN crystals in alkaline solutions," Journal of crystal Growth 287:376-380 (Jan. 2006).
- Zhong et al., "Demonstration of High Power Blue-Green Light Emitting Diode on Semipolar (1122) Bulk GaN Substrate," 2007, Electron Letter, vol. 43, No. 15, pp. 825-826.
- Zhong et al., "High Power and High Efficiency Blue Light Emitting Diode on Freestanding Semipolar (1122) Bulk GaN Substrate," 2007, Applied Physics Letter, vol. 90, No. 23, pp. 233504-233504-3.
- Chiang et al., "Luminescent Properties of Cerium-Activated Garnet Series Phosphor: Structure and Temperature Effects," Journal of the Electrochemical Society 155:B517-B520 (2008).
- Chiu et al., "Synthesis and Luminescence Properties of Intensely Red-Emitting  $M5Eu(WO_4)_{4-x}(MoO_4)_x$  ( $M=Li, Na, K$ ) Phosphors," Journal of the Electrochemical Society 155:J71-J78 (2008).
- Ci et al., " $Ca_{1-x}Mo_{1-y}Nb_yO_4:Eu^{3+}$ : A novel red phosphor for white light emitting diodes," Journal of Physics 152:670-674 (2008).
- Happek "Development of Efficient UV-LED Phosphor Coatings for Energy Saving Solid State Lighting" University of Georgia (Jan. 2007).
- Höppe et al., "Luminescence in  $Eu^{2+}$ -doped  $Ba_2Si_5N_8$ : fluorescence, thermoluminescence, and upconversion," Journal of Physics and Chemistry of Solids 61:2001-2006 (2000).
- Li et al., "The effect of replacement of Sr by Ca on the structural and luminescence properties of the red-emitting  $Sr_2Si_5N_8:Eu^{2+}$  LED conversion phosphor," Journal of Solid State Chemistry 181:515-524 (2008).
- Mueller-Mach et al., "Highly efficient all-nitride phosphor-converted white light emitting diode," Physica Status Solidi (a) 202:1727-1732 (Jul. 2005).
- Setlur et al., "Crystal chemistry and luminescence of  $Ce^{3+}$ -doped  $(Lu_2CaMg_2)-Ca_2(Si, Ge)_3O_{12}$  and its use in LED based lighting," Chemistry of Materials 18: 3314-3322 (2006).
- Wang et al., "New red  $Y_{0.85}Bi_{0.1}Eu_{0.05}V_{1-y}M_yO_4$  ( $M=Nb, P$ ) phosphors for light-emitting diodes," Physica B: Condensed Matter 403:2071-2075 (Jun. 2008).
- Yamamoto "White LED phosphors: the next step," Proceeding of SPIE (2010).
- Yang et al., "Preparation and luminescence properties of LED conversion novel phosphors  $SrZnO_2:Sm$ ," Materials Letters 62:907-910 (Mar. 2008).
- Lide et al., 'Thermal Conductivity of Ceramics and Other Insulating Materials,' CRC Handbook of Chemistry and Physics, 91st Edition, 2010-2011, pp. 12-203 and 12-204.
- <http://www.matbase.com/material/non-ferrous-metals/other/molybdenum/properties>, Data Table for: Non-Ferrous Metals: Other Metals: Molybdenum.
- Pattison et al., 'Gallium Nitride Based Microcavity Light Emitting Diodes With  $2\lambda$  Effective Cavity Thickness', Applied Physics Letters, vol. 90, Issue 3, 031111 (2007) 3pg.
- USPTO Office Action for U.S. Appl. No. 12/133,364 dated Nov. 26, 2010.
- USPTO Office Action for U.S. Appl. No. 12/133,364 dated Jun. 1, 2011.
- USPTO Notice of Allowance for U.S. Appl. No. 12/133,364 dated Oct. 11, 2011.
- USPTO Office Action for U.S. Appl. No. 12/133,365 dated Jun. 9, 2011.
- USPTO Office Action for U.S. Appl. No. 12/133,365 dated Oct. 18, 2011.
- USPTO Office Action for U.S. Appl. No. 12/334,418 dated Apr. 5, 2011.
- USPTO Office Action for U.S. Appl. No. 12/334,418 dated Oct. 19, 2011.
- USPTO Office Action for U.S. Appl. No. 12/478,736 dated Sep. 27, 2011.
- USPTO Office Action for U.S. Appl. No. 12/478,736 dated Feb. 7, 2012.
- USPTO Notice of Allowance for U.S. Appl. No. 12/478,736 dated Apr. 23, 2012.
- USPTO Office Action for U.S. Appl. No. 12/484,095 dated Nov. 10, 2010.
- USPTO Office Action for U.S. Appl. No. 12/484,095 dated Jul. 8, 2011.
- USPTO Office Action for U.S. Appl. No. 12/497,969 dated Feb. 2, 2012.
- USPTO Office Action for U.S. Appl. No. 12/534,838 dated May 3, 2011.
- USPTO Office Action for U.S. Appl. No. 12/534,838 dated Jan. 13, 2012.
- USPTO Office Action for U.S. Appl. No. 12/534,838 dated Mar. 20, 2012.
- USPTO Notice of Allowance for U.S. Appl. No. 12/534,838 dated Jun. 8, 2012.
- USPTO Office Action for U.S. Appl. No. 12/534,844 dated Sep. 16, 2010.
- USPTO Office Action for U.S. Appl. No. 12/534,844 dated Feb. 2, 2011.
- USPTO Office Action for U.S. Appl. No. 12/534,857 dated Sep. 1, 2010.
- USPTO Notice of Allowance for U.S. Appl. No. 12/534,857 dated May 27, 2011.
- USPTO Office Action for U.S. Appl. No. 12/546,458 dated Jul. 20, 2011.
- USPTO Notice of Allowance for U.S. Appl. No. 12/546,458 dated Nov. 28, 2011.
- USPTO Office Action for U.S. Appl. No. 12/556,558 dated Sep. 16, 2010.
- USPTO Notice of Allowance for U.S. Appl. No. 12/556,558 dated Mar. 22, 2011.
- USPTO Office Action for U.S. Appl. No. 12/556,562 dated Sep. 15, 2010.
- USPTO Office Action for U.S. Appl. No. 12/556,562 dated Mar. 21, 2011.
- USPTO Notice of Allowance for U.S. Appl. No. 12/556,562 dated Jul. 27, 2011.
- USPTO Office Action for U.S. Appl. No. 12/569,337 dated May 9, 2012.
- USPTO Office Action for U.S. Appl. No. 12/569,841 dated Dec. 23, 2011.
- USPTO Office Action for U.S. Appl. No. 12/724,983 dated Mar. 5, 2012.
- USPTO Notice of Allowance for U.S. Appl. No. 12/754,886 dated May 17, 2012.
- USPTO Notice of Allowance for U.S. Appl. No. 12/754,886 dated Jun. 5, 2012.
- USPTO Notice of Allowance for U.S. Appl. No. 12/754,886 dated Jun. 20, 2012.
- USPTO Office Action for U.S. Appl. No. 12/785,404 dated Mar. 6, 2012.
- Choi et al., '2.51 microcavity InGaN light-emitting diodes fabricated by a selective dry-etch thinning process', Applied Physics Letters, 2007, 91(6), 061120.
- Weisbuch et al., 'Recent results and latest views on microcavity LEDs', Light-Emitting Diodes: Research, Manufacturing, and Applications VIII, ed. By S.A. Stockman et al., Proc. SPIE, vol. 5366, p. 1-19 (2004).
- USPTO Notice of Allowance for U.S. Appl. No. 12/478,736 dated Oct. 9, 2012.
- USPTO Office Action for U.S. Appl. No. 12/497,969 dated Jul. 5, 2012.
- USPTO Office Action for U.S. Appl. No. 12/534,843 dated Sep. 10, 2012.
- USPTO Notice of Allowance for U.S. Appl. No. 12/534,849 dated Jul. 31, 2012.
- USPTO Notice of Allowance for U.S. Appl. No. 12/569,337 dated Nov. 15, 2012.
- USPTO Office Action for U.S. Appl. No. 12/569,844 dated Oct. 12, 2012.
- USPTO Notice of Allowance for U.S. Appl. No. 12/785,404 dated Jul. 16, 2012.
- USPTO Office Action for U.S. Appl. No. 12/891,668 dated Sep. 25, 2012.

# US 8,461,071 B2

Page 5

---

USPTO Office Action for U.S. Appl. No. 13/025,833 dated Jul. 12, 2012.

USPTO Office Action for U.S. Appl. No. 13/041,199 dated Nov. 30, 2012.

USPTO Office Action for U.S. Appl. No. 13/175,739 dated Dec. 7, 2012.

USPTO Office Action for U.S. Appl. No. 13/179,346 dated Aug. 17, 2012.

USPTO Office Action for U.S. Appl. No. 13/179,346 dated Dec. 13, 2012.

USPTO Office Action for U.S. Appl. No. 13/226,249 dated Oct. 10, 2012.

USPTO Notice of Allowance for U.S. Appl. No. 13/425,304 dated Aug. 22, 2012.

\* cited by examiner

Fig. 1

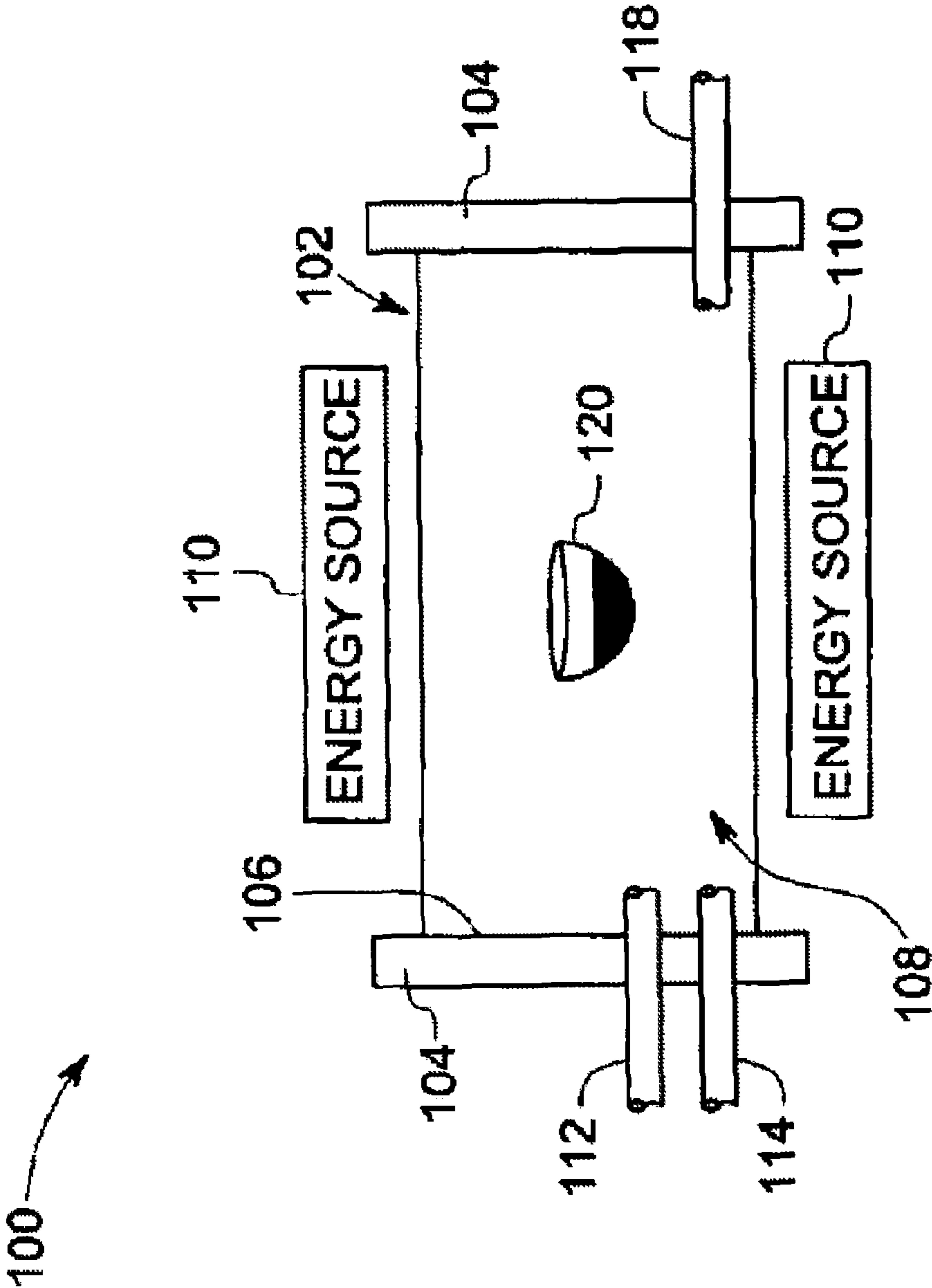
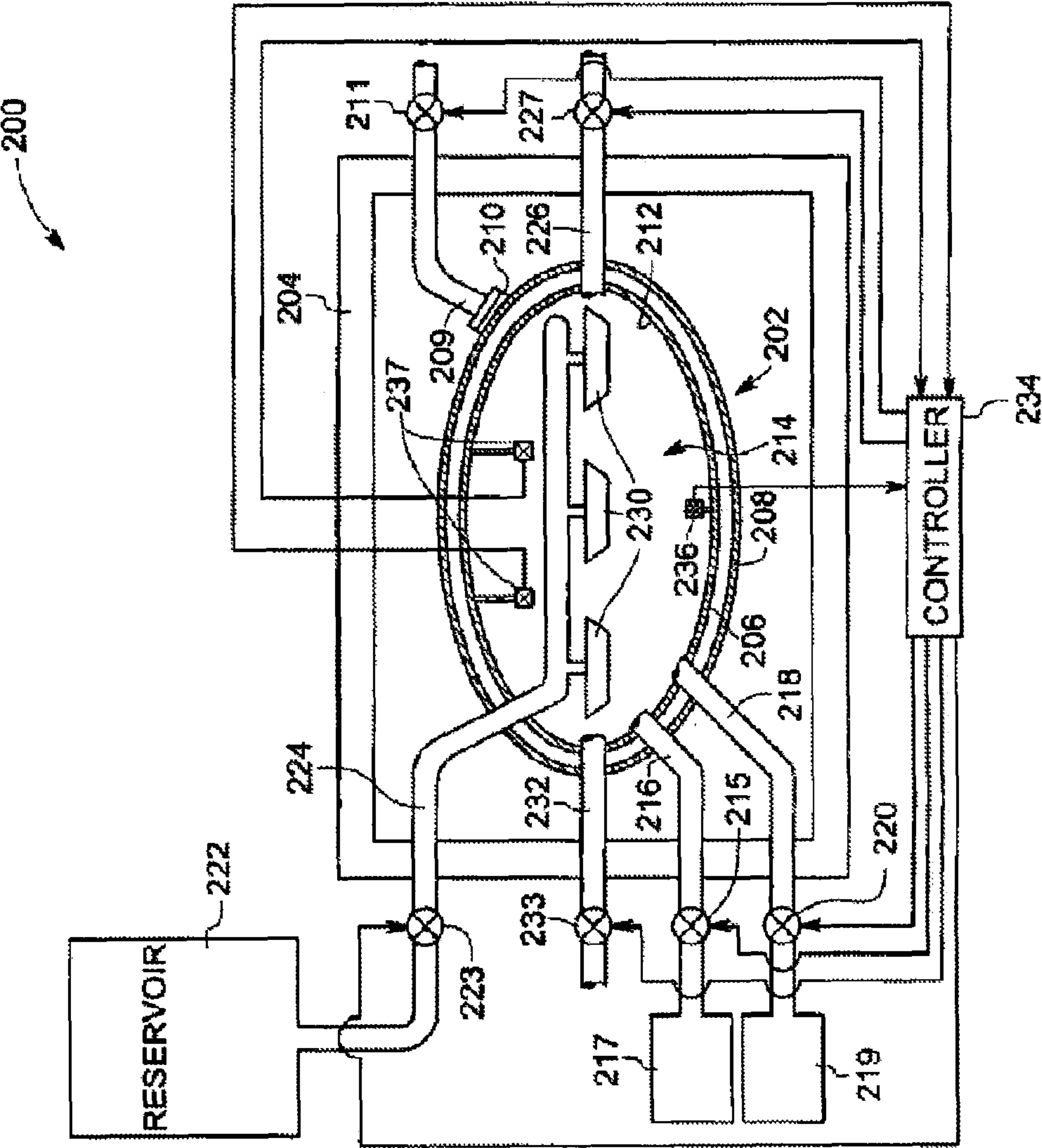




Fig. 2



მ  
ბ  
ქ

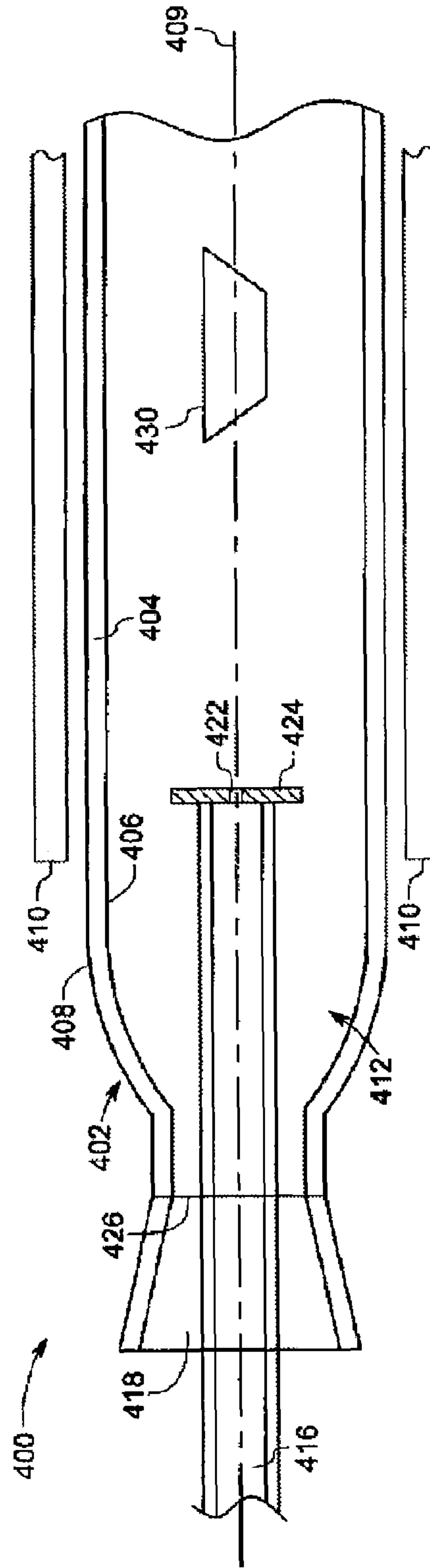




Fig. 4

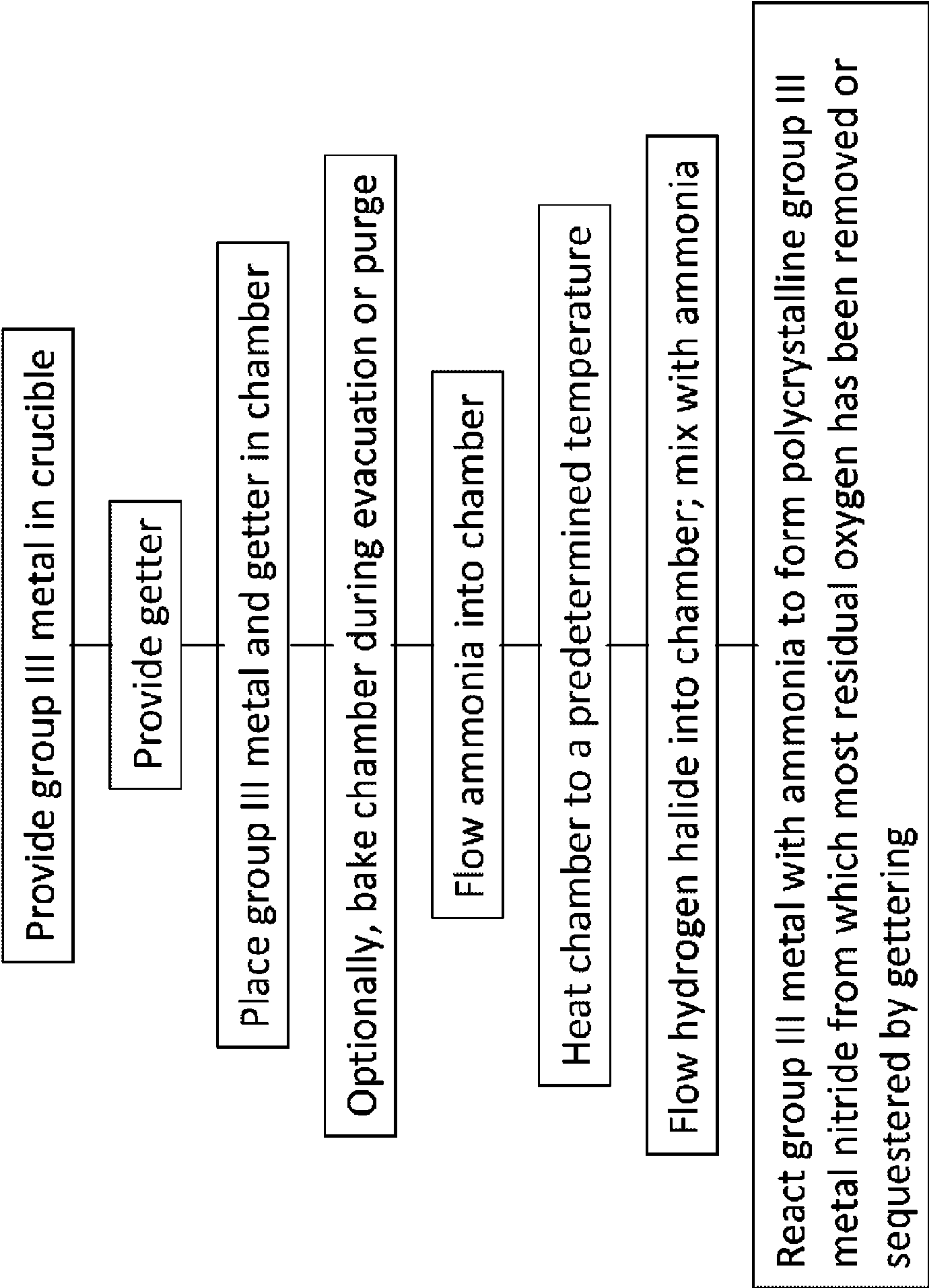
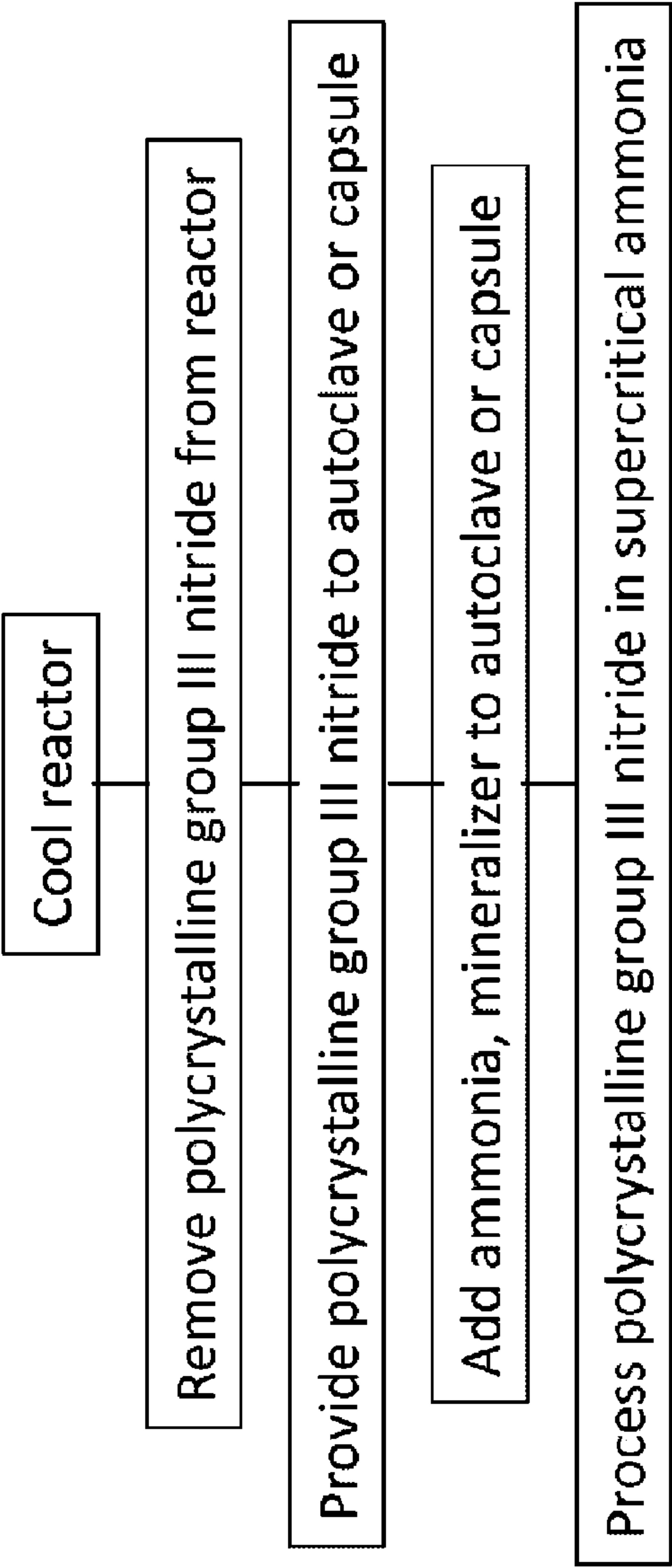


Fig. 5





# POLYCRYSTALLINE GROUP III METAL NITRIDE WITH GETTER AND METHOD OF MAKING

## CROSS-REFERENCES TO RELATED APPLICATIONS

This application claims priority to Provisional Patent Application No. 61/122,332, filed Dec. 12, 2008, commonly assigned, and incorporated by reference herein for all purpose.

## BACKGROUND OF THE INVENTION

The present invention generally relates to processing of materials for growth of crystals. More particularly, the present invention provides a crystalline nitride material suitable for use as a raw material for crystal growth of a gallium-containing nitride crystal by an ammonobasic or ammonoacidic technique, but there can be others. In other embodiments, the present invention provides methods suitable for synthesis of polycrystalline nitride materials, but it would be recognized that other crystals and materials can also be processed. Such crystals and materials include, but are not limited to, GaN, AlN, InN, InGaN, AlGaIn, and AlInGaIn, and others for manufacture of bulk or patterned substrates. Such bulk or patterned substrates can be used for a variety of applications including optoelectronic devices, lasers, light emitting diodes, solar cells, photoelectrochemical water splitting and hydrogen generation, photodetectors, integrated circuits, and transistors, among other devices.

Gallium nitride containing crystalline materials serve as substrates for manufacture of conventional optoelectronic devices, such as blue light emitting diodes and lasers. Such optoelectronic devices have been commonly manufactured on sapphire or silicon carbide substrates that differ in composition from the deposited nitride layers. In the conventional Metal-Organic Chemical Vapor Deposition (MOCVD) method, deposition of GaN is performed from ammonia and organometallic compounds in the gas phase. Although successful, conventional growth rates achieved make it difficult to provide a bulk layer of GaN material. Additionally, dislocation densities are also high and lead to poorer optoelectronic device performance.

Growth of nitride crystals by ammonothermal synthesis has been proposed. Ammonothermal crystal growth methods are expected to be scalable, as described by Dwilinski et al. [J. Crystal Growth 310, 3911 (2008)], by Ehrentraut, et al. [J. Crystal Growth 305, 204 (2007)], by D'Evelyn, et al. [J. Crystal Growth 300, 11 (2007)], and by Wang, et al. [Crystal Growth & Design 6, 1227 (2006)]. The ammonothermal method generally requires a polycrystalline nitride raw material, which is then recrystallized onto seed crystals. An ongoing challenge of ammonothermally-grown GaN crystals is a significant level of impurities, which cause the crystals to be colored, e.g., yellowish, greenish, grayish, or brownish. The residual impurities may cause optical absorption in light emitting diodes fabricated on such substrates, negatively impacting efficiency, and may also degrade the electrical conductivity and/or generate stresses within the crystals. One source of the impurities is the polycrystalline nitride raw material.

For example, gallium nitride crystals grown by hydride vapor phase epitaxy, a relatively more expensive, vapor phase method, have demonstrated very good optical transparency, with an optical absorption coefficient below  $2\text{ cm}^{-1}$  at wavelengths between about 385 nanometers and about 620 nanom-

eters [Oshima, et al., J. Appl. Phys. 98, 103509 (2005)]. However, the most transparent ammonothermally-grown gallium nitride crystals of which we are aware were yellowish and had an optical absorption coefficient below  $5\text{ cm}^{-1}$  over the wavelength range between about 465 nanometers and about 700 nanometers [D'Evelyn, et al., J. Crystal Growth 300, 11 (2007) and U.S. Pat. No. 7,078,731].

Several methods for synthesis of polycrystalline nitride materials have been proposed. Callahan, et al. [MRS Internet J. Nitride Semicond. Res. 4, 10 (1999); U.S. Pat. No. 6,406,540] proposed a chemical vapor reaction process involving heating gallium metal in a vapor formed by heating  $\text{NH}_4\text{Cl}$ . Related methods have been discussed by Wang, et al. [J. Crystal Growth 286, 50 (2006)] and by Park, et al. [U.S. Patent applications 2007/0142204, 2007/0151509 and 2007/0141819], all of which are hereby incorporated by reference in their entirety. The predominant impurity observed was oxygen, at levels varying from about 16 to about 160 parts per million (ppm). The chemical form of the oxygen was not specified. An alternative method, involving heating in ammonia only and producing GaN powder with an oxygen content below 0.07 wt %, was disclosed by Tsuji [U.S. Patent application 2008/0193363], which is hereby incorporated by reference in its entirety. Yet another alternative method, involving contacting Ga metal with a wetting agent such as Bi and heating in ammonia only, producing GaN powder with an oxygen content below 650 ppm, has been disclosed by Spencer, et al. [U.S. Pat. No. 7,381,391], which is hereby incorporated by reference in its entirety.

What is needed is a method for low-cost manufacturing of polycrystalline nitride materials that are suitable for crystal growth of bulk gallium nitride crystals and do not contribute to impurities in the bulk crystals.

## BRIEF SUMMARY OF THE INVENTION

According to the present invention, techniques related to processing of materials for growth of crystals are provided. More particularly, the present invention provides a crystalline nitride material suitable for use as a raw material for crystal growth of a gallium-containing nitride crystal by an ammonobasic or ammonoacidic technique, but there can be others. In other embodiments, the present invention provides methods suitable for synthesis of polycrystalline nitride materials, but it would be recognized that other crystals and materials can also be processed. Such crystals and materials include, but are not limited to, GaN, AlN, InN, InGaN, AlGaIn, and AlInGaIn, and others for manufacture of bulk or patterned substrates. Such bulk or patterned substrates can be used for a variety of applications including optoelectronic devices, lasers, light emitting diodes, solar cells, photoelectrochemical water splitting and hydrogen generation, photodetectors, integrated circuits, and transistors, among other devices.

In a specific embodiment, the present invention provides a composition for a material. The composition includes a polycrystalline group III metal nitride material having a plurality of grains. Preferably, the plurality of grains are characterized by a columnar structure. In a specific embodiment, one or more of the grains have an average grain size in a range of from about 10 nanometers to about 1 millimeter. The composition has an atomic fraction of a group III metal in the group III metal nitride in a range of from about 0.49 to about 0.55. In one or more embodiments, the metal in the group III metal nitride is selected from at least aluminum, indium, or gallium. The composition also has an oxygen content in the group III metal nitride material provided as a group III metal oxide or



3

as a substitutional impurity within a group III metal nitride is less than about 10 parts per million (ppm).

In an alternative specific embodiment, the present invention provides a method for forming a crystalline material. The method includes providing a group III metal in at least one crucible. Preferably, the group III metal comprises at least one metal selected from at least aluminum, gallium, and indium. The method includes providing a getter at a level of at least 100 ppm with respect to the group III metal. In a specific embodiment, the getter is selected from at least alkaline earth metals, scandium, titanium, vanadium, chromium, yttrium, zirconium, niobium, rare earth metals, hafnium, tantalum, and tungsten. The method also includes providing the group III metal in the crucible and the getter into a chamber. The method transfers a nitrogen-containing material into the chamber and heats the chamber to a determined temperature. The method includes pressurizing the chamber to a determined pressure and processing the nitrogen-containing material with the group III metal in the chamber. In one or more embodiments, the method forms a polycrystalline group III metal nitride in at least the crucible that contained the group III metal.

In yet an alternative specific embodiment, the present invention provides an alternative method of forming a group III metal nitride containing substrate. The method includes providing a group III metal as a source material, which comprises at least one metal selected from at least aluminum, gallium, and indium. The method includes providing a getter at a level of at least 100 ppm with respect to the group III metal source material and providing the group III metal source material and the getter into a chamber. The method also includes transferring a nitrogen-containing material into the chamber and heating the chamber to a determined temperature. In a preferred embodiment, the method includes pressurizing the chamber to a determined pressure and processing the nitrogen-containing material with the group III metal source material in the chamber. In one or more embodiments, the method forms a crystalline group III metal nitride characterized by a wurtzite structure substantially free from any cubic entities and an optical absorption coefficient of about  $2\text{ cm}^{-1}$  and less at wavelengths between about 385 nanometers and about 750 nanometers.

Still further, the present invention provides a gallium nitride containing crystal. The crystal has a crystalline substrate member having a length greater than about 5 millimeters and a substantially wurtzite structure characterized to be substantially free of other crystal structures. In a preferred embodiment, the other structures are less than about 1% in volume in reference to a volume of the substantially wurtzite structure. The crystal also has an impurity concentration greater than  $10^{15}\text{ cm}^{-1}$  of at least one of Li, Na, K, Rb, Cs, Mg, Ca, F, and Cl and an optical absorption coefficient of about  $2\text{ cm}^{-1}$  and less at wavelengths between about 385 nanometers and about 750 nanometers.

Benefits are achieved over pre-existing techniques using the present invention. In particular, the present invention enables a cost-effective manufacture of crystals that serve as a starting material for high quality gallium nitride containing crystal growth. In a specific embodiment, the present method and apparatus can operate with components that are relatively simple and cost effective to manufacture, such as ceramic and steel tubes. A specific embodiment also takes advantage of a getter material suitable for processing one or more chemicals for manufacture of high quality gallium nitride starting material. Depending upon the embodiment, the present apparatus and method can be manufactured using conventional materials and/or methods according to one of ordinary skill in the

4

art. In preferred embodiments, the final crystal structure is substantially clear and free of haze and other features that may be undesirable. Depending upon the embodiment, one or more of these benefits may be achieved. These and other benefits may be described throughout the present specification and more particularly below.

The present invention achieves these benefits and others in the context of known process technology. However, a further understanding of the nature and advantages of the present invention may be realized by reference to the latter portions of the specification and attached drawings.

#### BRIEF DESCRIPTION OF THE DRAWINGS

FIGS. 1, 2, and 3 are schematic diagrams illustrating reactors according to embodiments of the present invention;

FIG. 4 is a simplified flow diagram of a synthesis method according to an embodiment of the present invention; and

FIG. 5 is a simplified flow diagram of utilization method according to an embodiment of the present invention.

#### DETAILED DESCRIPTION OF THE INVENTION

According to the present invention, techniques related to processing of materials for growth of crystals are provided. More particularly, the present invention provides a crystalline nitride material suitable for use as a raw material for crystal growth of a gallium-containing nitride crystal by an ammonobasic or ammonoacidic technique, but there can be others. In other embodiments, the present invention provides methods suitable for synthesis of polycrystalline nitride materials, but it would be recognized that other crystals and materials can also be processed. Such crystals and materials include, but are not limited to, GaN, AlN, InN, InGaN, AlGaN, and AlInGaN, and others for manufacture of bulk or patterned substrates. Such bulk or patterned substrates can be used for a variety of applications including optoelectronic devices, lasers, light emitting diodes, solar cells, photoelectrochemical water splitting and hydrogen generation, photodetectors, integrated circuits, and transistors, among other devices.

The invention includes embodiments that may relate to a crystalline composition. The invention includes embodiments that may relate to an apparatus for making a crystalline composition. The invention includes embodiments that may relate to a method of making and/or using the crystalline composition.

Approximating language, as used herein throughout the specification and claims, may be applied to modify any quantitative representation that could permissibly vary without resulting in a change in the basic function to which it may be related. Accordingly, a value modified by a term such as "about" may be not to be limited to the precise value specified. In at least one instance, the variance indicated by the term about may be determined with reference to the precision of the measuring instrumentation. Similarly, "free" may be combined with a term; and, may include an insubstantial number, or a trace amount, while still being considered free of the modified term unless explicitly stated otherwise.

According to one embodiment of the invention, a composition of a polycrystalline metal nitride is provided. The polycrystalline metal nitride may have a plurality of grains, and these grains may have a columnar structure. In some embodiments, many grains may be bonded to one another, forming a polycrystalline plate. In other embodiments, a smaller number of grains may be bonded to one another, forming a polycrystalline powder.



## 5

With reference to the grains, the grains may be characterized by one or more properties. The properties may include a grain dimension. Other properties may include an average number of grains per unit volume, an inter-grain bend strength or a tilt angle of the grains relative to each other.

The grain dimension may refer to either an average grain size or an average grain diameter. The grains may have a columnar structure; in this case they have a major axis, and the average grain size refers to an average length of the grains along the major axis. Perpendicular to the major axis may be one or more minor axes, and the average diameter of each grain may be determined with reference to the minor axes. Collectively, the average diameters of each of the grains may be aggregated and averaged to provide the average grain diameter. An average, as used herein, may refer to the mean value.

The average grain size of the polycrystalline metal nitride may be in a range of greater than about 10 nanometers. In one embodiment, the average grain size may be in a range of from about 0.01 micrometer to about 1 millimeter, while in certain other embodiments, the grain size may be in a range of from about 0.01 micrometer to about 30 micrometers, from about 30 micrometers to about 50 micrometers, from about 50 micrometers to about 100 micrometers, from about 100 micrometers to about 500 micrometers, from about 500 micrometers to about 1 millimeter, or greater than about 1 millimeter. The average grain diameter may be larger than about 10 micrometers. In one embodiment, the average grain diameter may be in a range of from about 10 micrometers to about 20 micrometer, from about 20 micrometers to about 30 micrometers, from about 30 micrometers to about 50 micrometers, from about 50 micrometers to about 100 micrometers, from about 100 micrometers to about 500 micrometers, from about 500 micrometers to about 1 millimeter, or greater than about 1 millimeter.

An average number of grains per unit volume of the crystalline composition may indicate a grain average or granularity. The composition may have an average number of grains per unit volume of greater than about 100 per cubic centimeter. In one embodiment, the average number of grains per unit volume may be in a range of from about 100 per cubic centimeter to about 1000 per cubic centimeter, from about 1000 per cubic centimeter to about 10,000 per cubic centimeter, from about 10,000 per cubic centimeter to about  $10^5$  per cubic centimeter, or greater than about  $10^5$  per cubic centimeter.

The grains may be oriented at a determined angle relative to each other. The orientation may be referred to as the tilt angle, which may be greater than about 1 degree. In one embodiment, the grain orientation or tilt angle may be in a range of from about 1 degree to about 3 degrees, from about 3 degrees to about 5 degrees, from about 5 degrees to about 10 degrees, from about 10 degrees to about 15 degrees, from about 15 degrees to about 30 degrees, or greater than about 30 degrees.

Properties that are inherent in or particular to one or more crystalline articles produced according to an embodiment of the invention may include bend strength, density, moisture resistance, and porosity, among others. The properties may be measured using the corresponding ASTM standard test. Example of the ASTM standard test may include ASTM C1499.

The inter-grain bend strength of a film comprising one or more of crystals may be greater than about 20 MegaPascal (MPa). In one embodiment, the inter-grain bend strength may be in a range of from about 20 MegaPascal to about 50 MegaPascal, from about 50 MegaPascal to about 60 MegaPascal, from about 60 MegaPascal to about 70 MegaPascal,

## 6

from about 70 MegaPascal to about 75 MegaPascal, from about 75 MegaPascal to about 80 MegaPascal, from about 80 MegaPascal to about 90 MegaPascal, or greater than about 90 MegaPascal. The bend strength may indicate the grain to grain relationship at the inter-grain interface and/or the inter-grain strength.

The apparent density of crystalline articles may be greater than about 1 gram per cubic centimeter (g/cc). In one embodiment, the density may be in a range of from about 1 gram per cubic centimeter to about 1.5 grams per cubic centimeter, from about 1.5 grams per cubic centimeter to about 2 grams per cubic centimeter, from about 2 grams per cubic centimeter to about 2.5 grams per cubic centimeter, from about 2.5 grams per cubic centimeter to about 3 grams per cubic centimeter, or greater than about 3 grams per cubic centimeter. The crystalline composition density may be a function of, for example, the porosity or lack thereof, the crystal packing arrangement, and the like.

The crystalline article may be aluminum nitride and may have an apparent density of less than about 3.26 gram per cubic centimeter at standard test conditions. In one embodiment, the aluminum nitride crystalline article may have an apparent density in a range of from about 3.26 gram per cubic centimeter to about 2.93 gram per cubic centimeter, from about 2.93 gram per cubic centimeter to about 2.88 gram per cubic centimeter, from about 2.88 gram per cubic centimeter to about 2.5 gram per cubic centimeter, from about 2.5 gram per cubic centimeter to about 1.96 gram per cubic centimeter, or less than about 1.96 gram per cubic centimeter.

The crystalline article may be gallium nitride and may have an apparent density of less than about 6.1 gram per cubic centimeter at standard test conditions. In one embodiment, the gallium nitride crystalline article may have an apparent density in a range of from about 6.1 gram per cubic centimeter to about 5.49 gram per cubic centimeter, from about 5.49 gram per cubic centimeter to about 4.88 gram per cubic centimeter, from about 4.88 gram per cubic centimeter to about 4.27 gram per cubic centimeter, from about 4.27 gram per cubic centimeter to about 4 gram per cubic centimeter, or less than about 4 gram per cubic centimeter.

The porosity of the polycrystalline composition may be in a range of less than about 30 percent by volume. In one embodiment, the porosity may be in a range of from about 30 percent to about 10 percent, from about 10 percent to about 5 percent, from about 5 percent to about 1 percent, from about 1 percent to about 0.1 percent, or less than about 0.1 percent by volume.

The metal of the metal nitride may include a group III metal. Suitable metals may include one or more of aluminum, gallium, or indium. The "one or more" refers to combination of metals in the metal nitride, and may include compositions such as aluminum gallium nitride (AlGa<sub>2</sub>N), indium gallium nitride (InGa<sub>2</sub>N), aluminum indium nitride (AlIn<sub>2</sub>N), aluminum indium gallium nitride (AlInGa<sub>2</sub>N), and the like.

A fraction of the metal, or metals, in the metal nitride may be selected such that there is no excess metal in the metal nitride. In one embodiment, the atomic fraction of the metal may be greater than about 49 percent. In another embodiment, the atomic fraction may be in a range of from about 49 percent to about 50 percent, from about 50 percent to about 51 percent, from about 51 percent to about 53 percent, from about 53 percent to about 55 percent, or greater than about 55 percent.

In some embodiments, the group III metal nitride comprises a powder. The particle size of the powder may be between about 0.1 micron and about 100 microns. Some powder particles may comprise single crystals. Some powder



particles may comprise at least two grains. In other embodiments, the group III metal nitride comprises a grit. The particle size of the grit may be between about 100 microns and about 10 millimeters. Some grit particles may comprise single crystals. Some grit particles may comprise at least two grains.

The metal nitride composition may contain one or more impurities. As used herein, and as is commonly used in the art, the term “impurity” refers to a chemical species that is distinct from the group III metal nitride that constitutes the majority composition of the polycrystalline metal nitride. Several classes of impurities may be distinguished, with respect to chemistry, atomic structure, intent, and effect. Impurities will generally comprise elements distinct from nitrogen, aluminum, gallium, and indium, including oxygen, carbon, halogens, hydrogen, alkali metals, alkaline earth metals, transition metals, and main block elements. The impurity may be present in a number of forms, with different atomic structure. In some cases, the impurity is present as an isolated atom or ion within the crystalline lattice of the group III metal nitride, for example, as a substitutional or interstitial impurity. In other cases, the impurity is present in a distinct phase, for example, as an inclusion within an individual group III metal nitride grain or within a grain boundary of the group III metal nitride. The impurity may be deliberately added, to enhance the properties of the group III metal nitride in some way, or may be unintentional. Finally, the impurity may or may not have a significant effect on the electrical, crystallographic, chemical, or mechanical properties of the group III metal nitride.

As used herein, and as is commonly used in the art, the term “dopant” refers to an impurity that is atomically dispersed within the group III metal nitride, for example, as a substitutional or interstitial impurity, and is typically added intentionally. With regard to dopants and dopant precursors (collectively “dopants” unless otherwise indicated), the electrical properties of the group III metal nitride composition may be controlled by adding one or more of such dopants to the above composition during processing. The dopant may also provide magnetic and/or luminescent properties to the group III metal nitride composition. Suitable dopants may include one or more of s or p block elements, transition metal elements, and rare earth elements. Suitable s and p block elements may include, for example, one or more of silicon, germanium, magnesium, or tin. Other suitable dopants may include one or more of transition group elements. Suitable transition group elements may include one or more of, for example, zinc, iron, or cobalt. Suitable dopants may produce an n-type material, a p-type material, or a semi-insulating material. In some embodiments, oxygen, whether added intentionally or unintentionally, also acts as a dopant.

Suitable dopant concentration levels in the polycrystalline composition may be greater than about  $10^{10}$  atoms per cubic centimeter. In one embodiment, the dopant concentration may be in a range of from about  $10^{10}$  atoms per cubic centimeter to about  $10^{15}$  atoms per cubic centimeter, from about  $10^{15}$  atoms per cubic centimeter to about  $10^{16}$  atoms per cubic centimeter, from about  $10^{16}$  atoms per cubic centimeter to about  $10^{17}$  atoms per cubic centimeter, from about  $10^{17}$  atoms per cubic centimeter to about  $10^{18}$  atoms per cubic centimeter, from about  $10^{18}$  atoms per cubic centimeter to about  $10^{21}$  atoms per cubic centimeter, or greater than about  $10^{21}$  atoms per cubic centimeter.

As used herein, the term “getter” refers to an impurity that is intentionally added and has a higher chemical affinity for an undesired impurity, for example, oxygen, than the principal metallic constituent of the composition, for example, gallium.

The getter may become incorporated into the polycrystalline group III metal nitride in the form of an inclusion, for example, as a metal nitride, a metal halide, a metal oxide, a metal oxyhalide, or as a metal oxynitride. Examples of suitable getters include the alkaline earth metals, scandium, titanium, vanadium, chromium, yttrium, zirconium, niobium, the rare earth metals, hafnium, tantalum, and tungsten, and their nitrides and halides. In some embodiments, the getter impurity can act as both a getter and a dopant, such as magnesium. In other cases, the getter impurity atom has a larger atomic or covalent diameter than gallium and does not become incorporated as a dopant at sufficient levels to modify the electrical properties of the group III metal nitride significantly, and therefore functions predominantly or exclusively as a getter. The getter may be present in the polycrystalline group III metal nitride at a level greater than 100 ppm, from about 100 ppm to about 200 ppm, from about 200 ppm to about 500 ppm, from about 500 ppm to about 0.1%, from about 0.1% to about 0.2%, from about 0.2% to about 0.5%, from about 0.5% to about 2%, from about 2% to about 10%, or greater than 10%. Parts per million (ppm) and “%” refer to “by weight” unless otherwise indicated.

In other cases, impurities are unintended and/or undesirable inclusions in the polycrystalline group III metal nitride, and may result from, for example, processing and handling. Other unintentional impurities may result from contaminants in raw materials. Some unintentional impurities may be more closely associated with select raw materials. In some embodiments, the unintentional impurity includes oxygen present as a substitutional impurity, or dopant, in the polycrystalline group III metal nitride at higher than the desired level. In other embodiments, the unintentional impurity includes oxygen present as a group III oxide inclusion, for example,  $\text{Ga}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ , and/or  $\text{In}_2\text{O}_3$ . The unintentional oxygen impurity may originate from residual oxygen in the metal raw material, from moisture or  $\text{O}_2$  present as an impurity in the gaseous raw materials used in the synthesis process, from moisture generated from outgassing of the reactor components during the synthesis process, or from an air leak in the reactor. In one embodiment, the oxygen content present as  $\text{Ga}_2\text{O}_3$  or as a substitutional impurity within gallium nitride may be less than about 10 parts per million (ppm). In another embodiment, the oxygen content present as  $\text{Ga}_2\text{O}_3$  or as a substitutional impurity within gallium nitride may be in a range of from about 10 parts per million to about 3 parts per million, from about 3 parts per million to about 1 part per million, from about 1 part per million to about 0.3 parts per million, from about 0.3 part per million to about 0.1 parts per million, or less than about 0.1 part per million.

Referring now to the apparatus that includes an embodiment of the invention, the apparatus may include sub systems, such as a housing, one or more supply sources, and a control system.

The housing may include one or more walls, components, and the like. The walls of the housing may be made of a metal, a refractory material, or a metal oxide. In one embodiment, the walls of the housing comprise at least one of fused silica, alumina, carbon, or boron nitride. In one embodiment, the housing may have an inner wall, and an outer wall spaced from the inner wall. An inner surface of the inner wall may define a chamber.

The walls of the housing may be configured (e.g., shaped or sized) with reference to processing conditions and the desired end use. The configuration may depend on the size and number of components, and the relative positioning of those components, in the chamber. The chamber may have a pre-determined volume. In one embodiment, the housing may be



cylindrical with an outer diameter in a range of from about 5 centimeters to about 1 meter, and a length of from about 20 centimeters to about 10 meters. The housing may be elongated horizontally, or vertically. The orientation of the elongation may affect one or more processing parameters. For example and as discussed in further detail below, for a horizontal arrangement, a series of crucibles may be arranged in a series such that a stream of reactants flow over the crucibles one after another. In such an arrangement, the concentration and composition of the reactant stream may differ at the first crucible in the series relative to the last crucible in the series. Of course, such an issue may be addressed with such configuration changes as rearrangement of the crucibles, redirection of the reactant stream, multiple reactant stream inlets, and the like.

A liner may be disposed on the inner surface of the inner wall along the periphery of the chamber. Suitable liner material may include graphite or metal. The liner and other inner surfaces may not be a source of undesirable contaminants. The liner may prevent or reduce material deposition on the inner surface of the inner wall. The liner may prevent or reduce etching of the walls of the housing by halides of getter metals. Failing the prevention of material deposition, the liner may be removable so as to allow the deposited material to be stripped from the inner wall during a cleaning process or replacement of the liner.

Because the inner wall may be concentric to and spaced from the outer wall, the space may define a pathway between the inner wall and the outer wall for environmental control fluid to flow therethrough. Suitable environmental control fluids that may be used for circulation may include inert gases. Environmental control fluid may include gas, liquid or supercritical fluid. An environmental control inlet may extend through the outer wall to the space. A valve may block the environmental control fluid from flowing through the inlet and into the pathway to circulate between the inner and outer walls. In one embodiment, the inlet may be part of a circulation system, which may heat and/or cool the environmental control fluid and may provide a motive force for the fluid. The circulation system may communicate with, and respond to, the control system. Flanges, such as those meant for use in vacuum systems, may provide a leak proof connection for the inlet.

Suitable components of the housing may include, for example, one or more inlets (such as raw material inlets and dopant inlets), outlets, filters, heating elements, cold walls, pressure responsive structures, crucibles, and sensors. Some of the components may couple to one or more of the walls, and some may extend through the walls to communicate with the chamber, even while the housing is otherwise sealed. The inlets and the outlet may further include valves.

The inlets and the outlet may be made from materials suitable for semiconductor manufacturing, such as electropolished stainless steel materials. The inlets and/or outlets may be welded to the respective wall, or may be secured to the wall by one or more metal-to-metal seals. Optionally, the inlets and/or outlets may include purifiers. In one embodiment, the purifier includes a getter material, for example a zirconium alloy which may react with the contaminants to form the respective nitrides, oxides and carbides, thus reducing the probability of contamination in the final product. In one embodiment, the purifiers may be placed in the inlets at the entrance to the chamber. For reactions utilizing large quantities of ammonia the main concern for contamination may be the presence of water due to hygroscopic nature of ammonia. The contamination of ammonia drawn from an ammonia tank may increase exponentially as the ammonia

tank empties and when 70 percent of ammonia is reached, the tank may be replaced. Alternatively, a point-of-use purifier may be utilized at the inlets. The use of a point-of-use purifier may help in controlling the contamination in ammonia thereby reducing ammonia wastage. Optionally, lower grade ammonia may be utilized along with the point-of-use purifier to obtain the required grade of about 99.9999 percent.

The shape or structure of the inlets and outlet may be modified to affect and control the flow of fluid therethrough. For example, an inner surface of the inlet/outlet may be rifled. The rifling may spin the gas flowing out through the ends and enhance mixing. In one embodiment, the inlets may be coupled together such that the reactants may pre-mix before they reach reaction zone or hot zone. Each of the inlets and outlets may have an inner surface that defines an aperture through which material can flow into, or out of, the chamber. Valve apertures may be adjustable from fully open to fully closed thereby allowing control of the fluid flow through the inlets and the outlets.

The inlets may be configured to promote mixing of the nitrogen-containing gas and the halide-containing gas upstream of the crucible(s), so as to promote uniform process conditions throughout the volume of the chamber. One or more of the inlets may contain one or more of baffles, apertures, fits, and the like, in order to promote mixing. The apertures, frits, and baffles may be placed within the chamber proximate to the hot zone or crucibles so as to control the flow of gas in the chamber, which may prevent or minimize the formation of solid ammonium halide. The apertures, frits, and baffles may be placed upstream of the nearest crucible, with a distance of separation that is in a range from about 2 cm to about 100 cm, in order for mixing to be complete prior to the onset of reaction with the contents of the crucible. The presence of apertures and baffles may promote higher gas velocities that promote mixing and inhibit back-flow of gases, preventing or minimizing the formation of solid ammonium halide.

One or more crucibles may be placed within the chamber. In one embodiment, the number of crucibles within the chamber is about 6. Depending on the configuration of the chamber, the crucibles may be arranged horizontally and/or vertically within the chamber. The crucible shape and size may be pre-determined based on the end usage of the metal nitride, the raw material types, and the processing conditions. For the polycrystalline composition to be useful as a sputter target, the size of the crucible may be relatively larger than the required size of the sputter target. The excess of the polycrystalline composition may be removed, for example, through etching or cutting to form the sputter target article. Such removal may eliminate surface contamination resulting from contact with the crucible material.

The crucible may withstand temperatures in excess of the temperature required for crystalline composition formation while maintaining structural integrity, and chemical inertness. Such temperatures may be, greater than about 200 degree Celsius, in a range of from about 200 degree Celsius to about 1200 degree Celsius, or greater than about 1200 degrees Celsius. Accordingly, refractory materials may be suitable for use in the crucible. In one embodiment, the crucible may include a refractory composition including an oxide, a nitride, or an oxynitride. The crucible may be formed from one or more of graphite, molybdenum, tungsten, or rhenium or from one or more of an oxide, a nitride, or an oxynitride of silicon, aluminum, magnesium, boron, or zirconium. In a preferred embodiment, the crucible is formed from a nonoxide material, such as boron nitride, silicon carbide, tantalum carbide, or a carbon material such as graphite.



## 11

In one embodiment, a removable graphite liner may be placed inside the crucible so as to facilitate easy removal of the polycrystalline composition. In some embodiments, a getter is added to the crucible in the form of a foil or liner. In one specific embodiment, the getter foil or liner is chosen from at least one of zirconium, hafnium, and tantalum. In another embodiment, the crucible composition comprises at least one getter.

A quantity of group III metal, comprising at least one of aluminum, gallium, and indium, may be placed in at least one crucible. The group III metal may be added in solid or liquid form. A getter, comprising at least one of the alkaline earth metals, scandium, titanium, vanadium, chromium, yttrium, zirconium, niobium, the rare earth metals, hafnium, tantalum, and tungsten, may be placed in the at least one crucible along with the group III metal. The getter may be added at a level greater than 100 ppm, greater than 300 ppm, greater than 0.1%, greater than 0.3%, greater than 1%, greater than 3%, or greater than 10% by weight with respect to the group III metal. The getter may be added in the form of a powder, grit, wire, or foil. The getter may be added in the form of a metal, a nitride, a halide, or a mixture or compound thereof. The getter may contain oxygen.

In one embodiment, at least one wetting agent is also added to the crucible, contacting the group III metal. As used herein, "wetting agent" refers to an element or a compound that facilitates the mixing of or a reaction between an otherwise immiscible liquid mixture at the interface of the two components. The wetting agent can be any metal that facilitates interfacial wetting of a binary liquid metal mixture and does not readily react to form covalent bonds with Group III elements. Any suitable and effective wetting agent compound can be employed. Suitable wetting agents include bismuth (Bi), lead (Pb), germanium (Ge), and tin (Sn). Other suitable wetting agents include antimony (Sb), tellurium (Te), and polonium (Po). The reaction mixture can also include a mixture of two or more wetting agents, in any proportion. The reaction mixture can include a wetting agent compound, such as organometallic compounds containing the wetting agent metal or inorganic compounds containing the wetting agent metal. Suitable wetting agent compounds include, e.g., halides, oxides, hydroxides, and nitrates. Many suitable and effective wetting agents and wetting agent compounds are disclosed, e.g., in Aldrich Handbook of Fine Chemicals, 2003-2004 (Milwaukee, Wis.). As used herein, bismuth, germanium, tin, and lead refer to elemental metals, alloys containing these metals, compounds containing these metals, and mixtures thereof. The Group III metal and the wetting agent can be present in a molar ratio of about 1:1 to about 500:1. Specifically, the Group III element and the wetting agent can be present in a molar ratios of about 2:1, about 5:1, about 20:1, about 100:1, or about 200:1.

Suitable sensors may include one or more of pressure sensors, temperature sensors, and gas composition sensors. The sensors may be placed within the chamber, and may communicate the process parameters in the chamber to the control system.

Suitable supply sources may include one or more of an energy source, a nitrogen-containing gas source, a carrier gas source, a halide-containing gas source, a raw material source (sometimes referred to as a reservoir), environmental control fluid source, and the like.

The energy source may be located proximate to the housing and may supply energy, such as thermal energy, plasma energy, or ionizing energy to the chamber through the walls. The energy source may be present in addition to, or in place of, the heating elements disclosed above. In one embodiment,

## 12

the energy source may extend along an outward facing surface of the outer wall of the housing. The energy source may provide energy to the chamber.

The energy source may be a microwave energy source, a thermal energy source, a plasma source, or a laser source. In one embodiment, the thermal energy may be provided by a heater. Suitable heaters may include one or more molybdenum heaters, split furnace heaters, three-zone split furnaces, or induction heaters.

Sensors may be placed within the chamber. The sensors may be capable of withstanding high temperature and elevated or reduced pressure in the chamber and be chemically inert. The sensors may be placed proximate to the crucible, and/or may be placed at the inlets. The sensors may monitor process conditions such as the temperature, pressure, gas composition and concentration within the chamber.

The nitrogen-containing gas source may communicate through a first inlet with the chamber. The nitrogen-containing gas source may include one or more filters, purifiers, or driers to purify and/or dry the nitrogen-containing gas. In one embodiment, the nitrogen-containing gas may be produced at the source. The purifier may be able to maintain purity levels of the nitrogen-containing gas up to or above semiconductor grade standards for purity. Suitable nitrogen-containing gases may include ammonia, diatomic nitrogen, and the like. Where the presence of carbon is not problematic, nitrogen-containing organics may be used.

Controlling the aperture of the associated valve allows control of the flow rate of the nitrogen-containing gas into the chamber. Unless otherwise specified, flow rate will refer to volumetric flow rate. Processing considerations, sample size, and the like may determine an appropriate flow rate of the gas. The flow rate of nitrogen-containing gas may be greater than about 10 (standard) cubic centimeters per minute. In one embodiment, the flow rate of nitrogen-containing gas may be in a range of from about 10 cubic centimeters per minute to about 100 cubic centimeters per minute, from about 100 cubic centimeters per minute to about 200 cubic centimeters per minute, from about 200 cubic centimeters per minute to about 500 cubic centimeters per minute, from about 500 cubic centimeters per minute to about 1200 cubic centimeters per minute, from about 1200 cubic centimeters per minute to about 2000 cubic centimeters per minute, from about 2000 cubic centimeters per minute to about 3000 cubic centimeters per minute, from about 3000 cubic centimeters per minute to about 4000 cubic centimeters per minute, from about 4000 cubic centimeters per minute to about 5000 cubic centimeters per minute, or greater than about 5000 cubic centimeters per minute. In some embodiments, the flow of the nitrogen-containing gas in units of volume per second is chosen to be greater than 1.5 times the volume of the group III metal. In some embodiments, the flow of the nitrogen-containing gas is supplied at a gas flow velocity of at least 0.1 centimeters per second on the surface of the group III metal, at a reaction temperature of at least 700 degrees Celsius and no greater than 1,200 degrees Celsius.

The carrier gas source may communicate with the chamber through an inlet, or may share the first inlet with the nitrogen-containing gas. Pre-mixing the nitrogen-containing gas with the carrier gas may dilute the nitrogen-containing gas to a determined level. Because the nitrogen-containing gas may be diluted with the carrier gas, which may be inert, the likelihood of formation of certain halide solids proximate to the first inlet in the chamber may be reduced. Suitable carrier gases may include one or more of argon, helium, or other inert gases. In one embodiment, the carrier gas inlet is positioned so that a stream of carrier gas may impinge on a stream of



13

nitrogen-containing gas exiting the first inlet. Dopants may be entrained in the carrier gas, in one embodiment, for inclusion in the polycrystalline composition.

A halide-containing gas source may communicate through a second inlet with the chamber. As with the nitrogen-containing gas source, the halide-containing gas source may include one or more filters, purifiers, driers, and the like, so that the halide-containing gas be purified and/or dried at the source. The halide-containing gas may be produced at the source. Suitable halide-containing gases may include hydrogen chloride and the like. In some embodiments, the halide-containing gas is omitted from the process.

Controlling the aperture of the associated valve allows control of the flow rate of the halide-containing gas into the chamber. Processing considerations, sample size, and the like, may determine an appropriate flow rate of the gas. The flow rate of halide-containing gas may be greater than about 10 (standard) cubic centimeters per minute. In one embodiment, the flow rate of halide-containing gas may be in a range of from about 10 cubic centimeters per minute to about 50 cubic centimeters per minute, from about 50 cubic centimeters per minute to about 100 cubic centimeters per minute, from about 100 cubic centimeters per minute to about 250 cubic centimeters per minute, from about 250 cubic centimeters per minute to about 500 cubic centimeters per minute, from about 500 cubic centimeters per minute to about 600 cubic centimeters per minute, from about 600 cubic centimeters per minute to about 750 cubic centimeters per minute, from about 750 cubic centimeters per minute to about 1000 cubic centimeters per minute, from about 1000 cubic centimeters per minute to about 1200 cubic centimeters per minute, or greater than about 1200 cubic centimeters per minute.

The halide-containing gas may flow into the chamber from the halide-containing gas source through the second inlet. As with the nitrogen-containing gas, the halide-containing gas may be pre-mixed with the carrier gas to dilute the halide-containing gas to a determined level. The dilution of the halide-containing gas with an inert, carrier gas may reduce the likelihood of formation of certain halide solids in the second inlet, proximate to the chamber. Such a formation might reduce or block the flow therethrough. Optionally, the carrier gas inlet may be positioned such that a stream of carrier gas may impinge on a stream of halide-containing gas exiting the second inlet or entering the chamber. In one embodiment, dopants may be entrained in the carrier gas for inclusion in the polycrystalline composition.

The halide-containing gas and the nitrogen-containing gas may be introduced into the chamber in a manner that determine properties of the polycrystalline composition. The manner may include simultaneous introduction at a full flow rate of each component fluid (gas, liquid, or supercritical fluid). Other suitable introduction manners may include pulsing one or more of the components, varying the concentration and/or flow rate of one or more components, or staggered introductions, for example, to purge the chamber with carrier gas.

The halide-containing gas and the nitrogen-containing gas inlets may be disposed such that the exit end is located in the hot zone in the chamber. In one embodiment, one or more inlet is located in a region of the chamber that, during use, has a temperature of greater than about 341 degree Celsius at 1 atmosphere, or a temperature in a range of from about 341 degree Celsius to about 370 degree Celsius, or greater than about 370 degrees Celsius.

The ratio of flow rate of the nitrogen-containing gas to the flow rate of the halide-containing gas may be adjusted to optimize the reaction. In one embodiment, the ratio of flow

14

rate of the nitrogen-containing gas to the flow rate of halide-containing gas may be in a range of from about 30:1 to about 15:1, from about 15:1 to about 1:1, from about 1:1 to about 1:10, or from about 1:10 to about 1:15.

The raw material source may communicate through the raw material inlet and into the crucible, which is in the chamber. As with the other sources, the raw material source may include one or more filters, driers, and/or purifiers. Particularly with reference to the raw material source, purity of the supplied material may have a disproportionately large impact or effect on the properties of the final polycrystalline composition. The raw material may be produced just prior to use and may be kept in an inert environment to minimize or eliminate contamination associated with atmospheric contact. If, for example, hygroscopic materials are used, or materials that readily form oxides, then the raw material may be processed and/or stored such that the raw material does not contact moisture or oxygen. Further, because the raw material can be melted and flowed into the chamber during processing, in one embodiment, differing materials may be used in a continuous process than might be available for use relative to a batch process. At least some of such differences are disclosed herein below.

Suitable raw materials may include one or more of gallium, indium, or aluminum. In one embodiment, the raw material may have a purity of 99.9999 percent or greater. In another embodiment, the purity may be greater than about 99.99999 percent. The raw material may be a gas; a liquid solution, suspension or slurry; or a molten liquid. The residual oxygen in the metal may further be reduced by heating under a reducing atmosphere, such as one containing hydrogen, or under vacuum.

While all of the materials needed for production may be sealed in the chamber during operation in one embodiment; in another embodiment, various materials may be added during the process. For example, the raw material may flow through the raw material inlet, out of an exit end, and into a crucible within the chamber. Where there is a plurality of crucibles, multiple raw material inlets, or one inlet having multiple exit ends, may be used to flow raw material into individual crucibles. In one embodiment, the raw material inlet may be mounted on a linear motion feed-through structure. Such feed-through structures may allow the translation of the exit end of the raw material inlet from crucible to crucible.

The flow and the flow rate of raw material to, and through, the raw material inlet may be controlled by a valve. The valve may be responsive to control signals from the control system. While the flow rate of the raw material may be determined based on application specific parameters, suitable flow rates may be larger than about 0.1 kilogram per hour. In one embodiment, the flow rate may be in a range of from about 0.1 kilogram per hour to about 1 kilogram per hour, from about 1 kilogram per hour to about 5 kilograms per hour, or greater than about 5 kilograms per hour.

The dopant inlet may be in communication with a reservoir containing dopants and the chamber. The reservoir may be made of material compliant to semiconductor grade standards. The reservoir may have provision to purify/dry the dopants. In one embodiment, the reservoir may have liners. The liners may prevent corrosion of the reservoir material, or reduce the likelihood of contamination of the dopants by the reservoir.

The dopant source may be separate, or may be co-located with one or more of the other materials being added during processing. If added separately, the dopants may flow directly into a crucible by exiting an end of the dopant inlet. As mentioned, the dopant may be introduced by pre-mixing



15

with, for example, the raw material, the carrier gas, the halide-containing gas, or the nitrogen-containing gas. Metering of the dopant may control the dopant concentration levels in the polycrystalline composition. Similarly, the placement of the dopant in the polycrystalline composition may be obtained by, for example, pulsing, cycling, or timing the addition of the dopant.

Suitable dopants may include dopant precursors. For example, silicon may be introduced as  $\text{SiCl}_4$ . Where carbon is a desired dopant, carbon may be introduced as a hydrocarbon, such as methane, methylene chloride, or carbon tetrachloride. Suitable dopants may include a halide or a hydride. In situations where carbon is a desired dopant, or an inconsequential contaminant, metals may be introduced as an organometallic compound. For example, magnesium may be introduced as  $\text{Mg}(\text{C}_5\text{H}_5)_2$ , zinc as  $\text{Zn}(\text{CH}_3)_2$ , and iron as  $\text{Fe}(\text{C}_5\text{H}_5)_2$ . The flow rate of dopant precursors may be greater than about 10 (standard) cubic centimeters per minute. In one embodiment, the flow rate of the dopant precursors may be in a range of from about 10 cubic centimeters per minute to about 100 cubic centimeters per minute, from about 100 cubic centimeters per minute to about 500 cubic centimeters per minute, from about 500 cubic centimeters per minute to about 750 cubic centimeters per minute, from about 750 cubic centimeters per minute to about 1200 cubic centimeters per minute, or greater than about 1200 cubic centimeters per minute. Alternatively, the dopant may be added in elemental form, for example, as an alloy with the raw material. Other suitable dopants may comprise one or more of Si, O, Ge, Be, Mg, Zn, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Y, Zr, Mo, Sn, Ce, Pr, Nd, Pm, Sm, Eu, Dy, Er, Tm, Yb, or Hf.

The outlet, and corresponding valve, may control the release of material that is inside of the chamber. The released material may be vented to atmosphere, or may be captured, for example, to recycle the material. The released material may be monitored for composition and/or temperature by an appropriate sensor mounted to the outlet. The sensor may signal information to the control system. Because contamination may be reduced by controlling the flow of material through the chamber in one direction, the polycrystalline composition may be removed from the chamber by an exit structure in the wall at the outlet side.

The outlet may be coupled to an evacuation system. The evacuation system may be capable of forming a low base pressure or a pressure differential in the chamber relative to the atmospheric pressure. Suitable base pressure may be lower than about  $10^{-7}$  millibar. In one embodiment, the base pressure may be in a range of from about  $10^{-7}$  millibar to about  $10^{-5}$  millibar, or greater than about  $10^{-5}$  millibar. In one embodiment, the pressure differential may be in a range of from about 50 Torr to about 1 Torr, from about 1 Torr to about  $10^{-3}$  Torr, from about  $10^{-3}$  Torr to about  $10^{-5}$  Torr, or less than about  $10^{-5}$  Torr. The evacuation may be used for pre-cleaning, or may be used during processing.

The outlet may be heated to a temperature, which may be maintained, that is greater than the temperature where the vapor pressure of an ammonium halide that might be formed during processing is greater than the process pressure, for example, one bar. By maintaining a temperature above the sublimation point of ammonium halide at the reactor pressure, the ammonium halide might flow into a trap or may be precluded from forming or solidifying near the outlet once formed.

The control system may include a controller, a processor in communication with the controller, and a wired or wireless

16

communication system that allows the controller to communicate with sensors, valves, sources, monitoring and evaluating equipments, and the like.

The sensors within the chamber may sense conditions within the chamber, such as the temperature, pressure, and/or gas concentration and composition, and may signal information to the controller. Flow rate monitors may signal information about the flow rate through the corresponding inlet or outlet to the controller. The controller (via the processor) may respond to the information received, and may control devices in response to the information and pre-determined instruction parameters. For example, the controller may signal the energy source to provide thermal energy to the chamber. The controller may signal one or more valves to open, close, or open to a determined flow level during the course of polycrystalline composition synthesis. The controller may be programmed to implement a method of growing polycrystalline compositions according to embodiments of the invention.

The resultant polycrystalline composition may be a group III metal nitride. The metal nitride may be doped to obtain one or more of an n-doped or a p-doped composition. The metal nitride may be a metallic, semiconducting, semi-insulating or insulating material. Further, each of these compositions may be a magnetic or a luminescent material.

The working of the apparatus and the function of the various components are described below with reference to illustrated embodiments. Referring to the drawings, the illustrations describe embodiments of the invention and do not limit the invention thereto.

An apparatus **100** in accordance with an embodiment is shown in FIG. 1. The apparatus **100** may be used for preparing a metal nitride material, and may include a housing **102** having a wall **104**. The wall **104** may have an inner surface **106** that defines a chamber **108**. An energy source **110** may be located proximate to the wall **104**. A first inlet **112** and a second inlet **114** extend through the wall **104**. The inlets **112**, **114** define an aperture through which material can flow into, or out of, the chamber **108**. An outlet **118** extends through the wall **104** to the chamber **108**. A crucible **120** may be disposed in the chamber **108**. A liner (not shown) may line the inner surface **106** of the wall **104**.

The energy source **110** may be a thermal energy source, such as a ceramic heater. The inlets **112**, **114** and the outlet **118** may be electro-polished stainless steel suitable for semiconductor grade manufacturing. In a specific embodiment, the crucible **120** may include boron nitride, and the inert liner may include graphite.

During operation, a group III metal raw material and a getter may be filled into the crucible **120**, and the crucible may be pre-loaded into the chamber. One or more dopants may be placed in the crucible with the raw material. After loading, the crucible **120** may be sealed by a sealing mechanism (not shown).

A nitrogen-containing gas may flow through the first inlet **112** into the chamber **108**. The nitrogen-containing gas may include ammonia, and may include a carrier gas for pre-dilution. A halide-containing gas may flow through the second inlet **114** and into the chamber **108**. The halide-containing gas may include hydrogen chloride. The halide-containing gas may be pre-diluted with a carrier gas. Unreacted gases and/or other waste materials may be removed from the chamber **108** through the outlet **118**. The chamber **108** may be purged by flowing in gases through the inlets **112**, **114** and out through the outlet **118** prior to, crystalline composition formation. The outflow, optionally, may



17

be monitored to detect the impurity level of the out-flowing gas, which may indicate when a sufficient purge has been achieved.

The energy source **110** may be activated. Activating the energy source **110** may increase the temperature within the chamber **108** to pre-determined level and at a pre-determined rate of temperature increase. An area, within the chamber **108** and proximate to the crucible **120**, may define a hot zone or reaction zone (not shown).

The raw material, already in the crucible **120**, may respond to contact with the nitrogen-containing gas in the presence of the halide-containing gas, and at the determined temperature, by reacting to form a nitride of the metal, that is, the polycrystalline composition.

Without wishing to be bound by theory, I believe that the group III metal reacts with a hydrogen halide to form a volatile group III metal halide. The group III metal halide in turn reacts with the nitrogen-containing gas, for example, ammonia, to form a polycrystalline group III metal nitride. Under typical processing conditions, most of the group III metal may react to form a polycrystalline group III metal nitride and only a small fraction of the group III metal may be transported away from the crucible in the form of a group III metal halide. Under typical reaction conditions, some, most, or all of the getter may be dissolved in the liquid group III metal. Many of the getters disclosed above are broadly miscible in liquid aluminum, gallium, or indium at temperatures above 500-1000 degrees Celsius. Even the refractory metals Zr, Hf, and Ta are soluble at a level above about 1-2% in gallium at 1000 degrees Celsius. The dissolved metal may become well mixed within the molten group III metal. The dissolved getter metal may react with dissolved oxygen within the molten group III metal, forming an oxide of the getter metal. Like the group III metal, the getter metal may form halides and/or nitrides. At temperatures of about 500 to 1000 degrees Celsius, the getter metal halides are relatively volatile and the getter metal nitrides, oxides, and oxynitrides are generally not volatile. In the case of some getters, for example, the alkaline earth metals and yttrium, the halides may be formed predominantly and most of the getter metal transported away from the crucible. During the reaction and transport process, however, the getter metal efficiently ties up or removes oxygen from the group III metal and from sources of oxygen in the gas phase, including O<sub>2</sub> and H<sub>2</sub>O. In the case of other getters, for example, Cr and Ta, the nitrides may be formed predominantly and most of the getter metal may remain in the crucible in the form of nitride, oxynitride, and oxide inclusions within the polycrystalline group III nitride. During the reaction and transport process, the getter metal efficiently ties up or removes oxygen from the group III metal and from sources of oxygen in the gas phase.

In some embodiments, including those not involving the addition of a hydrogen halide to the reaction, most or all of the getter may become incorporated into the polycrystalline group III nitride composition.

After the polycrystalline composition has been formed, the housing **102** may be opened at the outlet side. Opening on the outlet side may localize any introduced contaminants to the chamber **108** caused by the opening to the chamber side proximate to the outlet **118**. Localizing the contaminants proximate to the outlet **118** may reduce the distance the contaminants must travel to purge from the chamber **108**, and may confine the path of the contaminants to regions in which the contaminants are less likely to contact any grown crystal, or crystalline composition growing surface (such as an inner surface of the crucible **120**). In addition, not opening the housing on the inlet side may decrease the likelihood of a leak

18

proximate to the inlet during a subsequent run. Thus, such a configuration may reduce the chance of contaminants contaminating the produced crystals.

An apparatus **200** in accordance with an embodiment is shown in FIG. 2. The apparatus **200** may include a housing **202**, and an energy source **204** proximate to the housing **202**. The housing **202** may include an inner wall **206** and an outer wall **208**. An inlet **209** may extend through the outer wall **208**, but may stop short of the inner wall **206**. The outer wall **208** may have an outward facing surface. An inward facing surface or inner surface **212** of the inner wall **206** may define a chamber **214**.

The inner wall **206** may be nested within, and spaced from, the outer wall **208**. The space between the walls **206** and **208** may be used to circulate an environmental control fluid that may enter the space through the inlet **209** configured for that purpose. The outer wall **208** may be formed from metal, while the inner wall **206** may be made of quartz. The energy source **204** may be proximate to the outer wall **208**.

A first inlet **216**, a second inlet **218**, a raw material inlet **224**, a dopant inlet **232**, and an outlet **226** may extend through the inner and outer walls **206** and **208**. A plurality of valves **215**, **220**, **223**, **233** may be disposed, one per tube, within the feed tubes that extend from sources to the corresponding inlets **216**, **218**, **224**, and **232**. The individual feed tubes are not identified with reference numbers. And, the outlet **226** may have a valve **227** that may allow or block the flow of fluid therethrough.

The first inlet **216** may communicate with a nitrogen-containing gas source **217** and flow a nitrogen-containing gas into the chamber **214**. The nitrogen-containing gas may include ammonia. The nitrogen-containing gas may be diluted with a carrier gas. The carrier gas may be argon, and may be controllable separately from the nitrogen-containing gas flow. The second inlet **218** may be in communication with a halide-containing gas source **219**. The second inlet **218** may allow a halide-containing gas to flow from the halide-containing gas source **219** into the chamber **214**. The valve **220** may control the flow of the halide-containing gas from the halide-containing gas source **219** through the second inlet **218** and into the chamber **214**. The halide-containing gas may include hydrogen chloride, which may have been diluted with the carrier gas. The raw material inlet **224** may communicate with a raw material reservoir **222**. An exit end of the raw material inlet **224** may be positioned so as to flow raw material leaving the inlet **224** into a crucible **230**. The valve **223** may control the flow of the raw material from the reservoir **222** through the raw material inlet **224** and into the chamber **214**. The raw material may include molten gallium.

The dopant source (not shown) may communicate with the chamber **214** through the dopant inlet **232**. The valve **233** may be switched on/off to open or block a flow of dopant from the dopant source into the chamber **214**. In the illustrated embodiment, the dopant includes silicon, which may be in the form of SiCl<sub>4</sub>.

The outlet **226** may allow for excess material to exit the chamber **214**. The valve **227** may open or close, and by closing, a back pressure might be built up as additional materials are flowed into the chamber **214** and the temperature is increased.

A plurality of crucibles **230** may be provided in the chamber **214**. The crucibles **230** may be arranged horizontally relative to each other. Sensors **236** and **237** may be provided to monitor the pressure and temperature, or other process parameters within the chamber **214**.

As disclosed hereinabove, the environmental control fluid may flow in the space between the walls through the inlet **209**.



19

The inlet **209** may communicate with a circulation system (not shown) to circulate the fluid in the space between the walls. The inlet **209** may include a valve **211** to adjust or optimize the circulation in the space between the walls. Flanges **210** meant for vacuum systems may be used to form a leak proof connection. The fluid circulation system may have provision to heat or cool the fluid. The chamber **214**, along with its contents, may be cooled or heated through this arrangement.

A control system may include a controller **234** that may communicate with the various components as indicated by the communication lines. Through the lines, the controller **234** may receive information, such as signals, from sensors **236**, **237**. The controller **234** may signal to one or more of the valves **215**, **220**, **223**, **227**, **233**, which may respond by opening or closing. The valve **211** may communicate with the controller **234**, and through which the controller **234** may control the flow of the environmental control fluid from the circulation system. Thus, the controller **234** may monitor and may control the overall reaction conditions.

Prior to operation, the chamber **214** may be evacuated. The controller **234** may activate the valve **227** and a vacuum pump (not shown) to evacuate the chamber **214**. The chamber **214** may be flushed with inert carrier gas. The energy source **204** may be activated to heat, and thereby volatilize, any volatile contaminants. The successive evacuation and purging may remove the contaminants from the chamber **214**.

During operation, the controller may activate the valve **223** to start a flow of raw material from the reservoir **222** to the crucibles **230** through the raw material inlet **224**. The dopant may be flowed into the crucible through the dopant inlet **232** in response to the opening of the corresponding valve **233**. The controller may adjust the rates of flow of materials by adjusting the degree to which the corresponding valves are open or closed. The controller **234** may communicate with the sensors **236**, **237**. The temperature and pressure within the chamber may be raised to determined levels by the controller **234** activating the energy source **204**, and/or adjusting the outlet valve **227**.

Once the desired temperature and pressure has been attained, the nitrogen-containing gas may be introduced in the chamber **214** through the first inlet **216**. Alternatively, the nitrogen-containing gas may be introduced in the chamber in the beginning of the heating cycle. The halide-containing gas may be flowed in through the second inlet **218**. The controller may adjust the flow rate of these gases by controlling the respective valves **215**, **220**.

The raw material including the dopants may react with the nitrogen-containing gas in the presence of the halide-containing gas. The reaction may proceed until the raw material reacts to form the metal nitride. In the illustrated embodiment, a silicon doped gallium nitride may be formed.

FIG. **3** is a schematic view of an apparatus **400** detailing the inlets in accordance with an embodiment. The apparatus **400** may include a housing **402** having a wall **404**, the wall **404** may have an inner surface **406** and an outward facing surface **408**, as illustrated in the figure. The wall **404** may be radially spaced from an axis **409**. An energy source **410** may be provided proximate to the outer surface **408**. The inner surface **406** of the wall **404** may define a chamber **412**.

The apparatus **400** may further include inlets **416** and **418**. The inlet **416**, in one embodiment, may be a single walled tube, and extends into the chamber **412** through the wall **404**. The inlet **416** may be nested within, and spaced from the inner surface **406** of the wall **404**. An exit end of the inlet **416** may define an aperture **422**. A baffle **424** may adjoin the aperture **422**. The spacing between the inlet **416** and the inner surface

20

**406** of the wall **404** may define the inlet **418**. Further, an aperture or opening **426** may be provided in the inlet **418**. A crucible **430** may be disposed within the chamber **412**.

A halide-containing gas may be introduced into the chamber **412** from a source (not shown) through the inlet **416**, and a nitrogen-containing gas may be introduced into the chamber **412** from a source (not shown) through the inlet **418**. The inlets **416** and **418** may be configured such that the baffle **424** provided in the inlet **416** may assist in proper mixing of the gases flowing in to the chamber **412** through the inlets.

The apparatus **400** may further include components not shown in the figure such as, a control system including a controller which may control the overall reaction, valves for adjusting and/or controlling the flow of materials to and/or from the chamber, inlets for introducing raw materials and/or dopants into the chamber, sources from where raw materials and/or dopants may be flowed into the chamber, sensors for monitoring the temperature, pressure and composition within the chamber, and the like. The working of the apparatus may be explained with reference to above described embodiments.

FIG. **4** is a flow chart depicting a method for preparing a polycrystalline group III metal nitride in accordance with an embodiment of the invention. The method starts by providing a group III metal and a getter in a crucible. The crucible containing the group III metal and the getter are then loaded into a chamber or reactor and the chamber is sealed. The chamber is then evacuated, purged, and otherwise decontaminated to remove trace impurities. The chamber may be evacuated, purged, and otherwise decontaminated prior to loading the group III metal and the getter inside. The environment in the chamber is adjusted to determined levels. The temperature of the chamber may be maintained between about 800 degree Celsius to about 1300 degree Celsius, and the pressure within the chamber may be greater than about ambient.

Dopants may be introduced in the chamber. The dopant may be introduced as a dopant precursor. The dopant precursor may be flowed into the chamber from a dopant source.

The temperature within the chamber may be raised to between about 800 degrees Celsius to about 1300 degrees Celsius, and the pressure may be raised to at least one dimension greater than about 1 meter, for a period greater than about 30 minutes. Next, a nitrogen-containing gas such as ammonia may be introduced in the chamber. The gas may be flowed from a nitrogen-containing gas source through an inlet into the chamber. The flow rate of the nitrogen-containing gas may be greater than about 250 (standard) cubic centimeters per minute.

A halide-containing gas may be introduced into the chamber. Optionally, the order of the preceding steps may be interchanged. The flow rate of the halide-containing gas may be greater than about 25 cubic centimeters per minute. The ratio of the flow rate of the nitrogen-containing gas to the flow rate of the halide-containing gas may be about 10:1.

The group III metal may react with the nitrogen-containing gas in the presence of the halide to form a polycrystalline group III metal nitride. The halide affects the reaction between the metal and the nitrogen-containing gas in a determined manner. The getter reacts with oxygen to form a getter metal oxide, oxynitride, or oxyhalide, and additionally with the nitrogen-containing gas to form getter metal nitride and with the hydrogen halide to form getter metal halide.

The reaction may proceed through a vapor transport and/or a wicking effect. The metal nitride crust may form on top of the molten metal within the crucible. The crust may be slightly porous. The metal may be vapor transported or, if liquid, wicked to the top of the crust through the pores and react with the nitrogen-containing gas. The reaction may



deposit additional metal nitride and add to the crust. The reaction proceeds until virtually all the metal has undergone reaction. Additional metal may be flowed into the chamber from the reservoir.

The chamber may be cooled, See FIG. 5, as an example. The excess nitrogen-containing gas and hydrogen halide flows out from the reaction zone and ammonium halide may condense on cooler regions of the chamber. In one embodiment, the outlet may be kept hot so as to facilitate downstream trapping of ammonium halide; or alternatively a cold wall section may be incorporated to facilitate condensation of the ammonium halide. The chamber may be opened on the outlet side to minimize leakage through the inlet side. The polycrystalline group III metal nitride may be removed through the outlet side.

Optionally, the polycrystalline group III metal nitride formed may be further processed. In one embodiment, at least one surface of the polycrystalline group III metal nitride may be subjected to one or more of scraping, scouring or scarifying. The surface may be further subjected to oxidation in air or in dry oxygen and it may further be boiled in perchloric acid. The residual contamination resulting from the post-processing step may be removed by washing, sonicating, or both. Washing and sonicating may be performed in, for example, organic solvents, acids, bases, oxidizers (such as hydrogen peroxide), and the like. The polycrystalline group III metal nitride may be annealed in an inert, nitriding, or reducing atmosphere. The annealing may also be performed in pure ammonia at a temperature of about 800 degree Celsius to about 1200 degree Celsius for a period of time in a range of from about 30 minutes to about 200 hours.

Other processing may be performed for use as a source material for crystalline composition growth. For use as a source material, the polycrystalline group III metal nitride may be pulverized into particulate. The particles may have an average diameter in a range of from about 0.3 millimeters to about 10 millimeters. The pulverizing may be carried out through, for example, compressive fracture, jaw crushing, wire sawing, ball milling, jet milling, laser cutting, or cryo-fracturing. Post pulverization cleaning operations may remove adventitious metal introduced by the pulverization operation, un-reacted metal, and undesirable metal oxide.

In some embodiments, the polycrystalline group III metal nitride is used as a source material for ammonothermal growth of at least one group III metal nitride single crystal. The polycrystalline group III metal nitride is placed in an autoclave or a capsule, as described in U.S. Pat. Nos. 6,656, 615, 7,125,453, and 7,078,731 and in U.S. patent application Ser. No. 12/133,365, each of which is incorporated by reference in their entirety. Ammonia and a mineralizer, for example, at least one of an alkali metal, amide, nitride, or azide, an alkaline earth metal, amide, nitride, or azide, ammonium fluoride, ammonium chloride, a group III metal fluoride, a group III metal chloride, or a reaction product between a group III metal, ammonia, HF, and HCl are also placed in the autoclave or capsule.

In some embodiments a getter is also placed in the autoclave or capsule. The added getter may be provided in addition to a getter composition that may be present in the polycrystalline group III nitride. The added getter may comprise at least one of alkaline earth metals, Sc, Ti, V, Cr, Y, Zr, Nb, Hf, Ta, W, rare earth metals, and their nitrides, halides, oxynitrides, oxyhalides, amides, imides, and azides. In one specific embodiment, at least a portion of the getter is added in the form of a metal and at least a portion of the mineralizer is added as an azide in such a ratio that the hydrogen generated by reaction of the getter metal with ammonia and the nitrogen

generated by decomposition of the azide are present in a ratio of approximately 3:1, as described in U.S. Patent Application No. 61/086,799, which is hereby incorporated by reference in its entirety. The added getter may be useful for removing unintentional impurities, for example, oxygen, that are present in the mineralizer or other raw material. In one set of embodiments, the mineralizer comprises an alkali metal and the getter comprises a nitride, imide, or amide of Be, Mg, Ca, Sr, Ba, Sc, Y, a rare earth metal, Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, or W. In another set of embodiments, the mineralizer comprises Cl and the getter comprises a nitride, chloride, oxynitride, or oxychloride of Sc, Cr, Zr, Nb, Hf, Ta, or W. In still another set of embodiments, the mineralizer comprises F and the getter comprises a nitride, fluoride, oxynitride, or oxy-fluoride of Cr, Zr, Nb, Hf, Ta, or W.

After all the raw materials have been added to the autoclave or capsule, the autoclave or capsule is sealed.

The capsule, if employed, is then placed within a suitable high pressure apparatus. In one embodiment, the high pressure apparatus comprises an autoclave, as described by U.S. Pat. No. 7,335,262, which is hereby incorporated by reference in its entirety. In another embodiment, the high pressure apparatus is an internally heated high pressure apparatus, as described in U.S. Pat. No. 7,125,453, and in U.S. Patent Applications 2006/0177362A1 and U.S. Ser. No. 12/133,364, which are hereby incorporated by reference in their entirety. The polycrystalline group III metal nitride is then processed in supercritical ammonia at a temperature greater than about 400 degrees Celsius and a pressure greater than about 0.2 gigaPascal (GPa), during which at least a portion of the polycrystalline group III metal nitride is etched away and recrystallized onto at least one group III nitride crystal with a wurtzite structure. In some embodiments, the polycrystalline group III metal nitride is processed in supercritical ammonia at a temperature greater than about 500 degrees Celsius, greater than about 550 degrees Celsius, greater than about 600 degrees Celsius, greater than about 650 degrees Celsius, greater than about 700 degrees Celsius, or greater than about 750 degrees Celsius. In some embodiments, the polycrystalline group III metal nitride is processed in supercritical ammonia at a pressure greater than about 0.3 GPa, greater than about 0.4 GPa, greater than about 0.5 GPa, greater than about 0.6 GPa, greater than about 0.7 GPa, or greater than about 0.8 GPa.

Residual getter in the polycrystalline group III metal nitride is released into solution gradually, as the polycrystalline group III metal nitride is etched. Once in solution, the getter may react to form a getter metal nitride, amide, or halide. The getter may also be chemically bound to oxygen. The getter may remove residual oxygen in the supercritical ammonia solution, enabling growth of group III nitride single crystals with improved purity.

In some embodiments, the added getter is annealed and/or coarsened prior to substantial ammonothermal growth of a group III metal nitride. In some embodiments, the getter may be added as a fine powder or may form a fine powder during heating in ammonia with a mineralizer present, which may undergo undesirable convection throughout the crystal growth environment and/or become incorporated into a crystalline group III metal nitride as an inclusion. The getter may be consolidated by holding at a temperature lower than that at which significant group III metal nitride crystal growth occurs, for example, between about 200 degrees Celsius and about 500 degrees Celsius, for a period of time between about 10 minutes and about 48 hours.

The ammonothermally-grown crystalline group III metal nitride may be characterized by a wurtzite structure substan-



tially free from any cubic entities and have an optical absorption coefficient of about  $2\text{ cm}^{-1}$  and less at wavelengths between about 385 nanometers and about 750 nanometers. An ammonothermally-grown gallium nitride crystal may comprise a crystalline substrate member having a length greater than about 5 millimeters, have a wurtzite structure and be substantially free of other crystal structures, the other structures being less than about 0.1% in volume in reference to the substantially wurtzite structure, an impurity concentration greater than  $10^{14}\text{ cm}^{-3}$ , greater than  $10^{15}\text{ cm}^{-3}$ , or greater than  $10^{16}\text{ cm}^{-3}$  of at least one of Li, Na, K, Rb, Cs, Mg, Ca, F, and Cl, and an optical absorption coefficient of about  $2\text{ cm}^{-1}$  and less at wavelengths between about 385 nanometers and about 750 nanometers. The ammonothermally-grown gallium nitride crystal may be semi-insulating, with a resistivity greater than  $10^7\text{ }\Omega\text{-cm}$ . The ammonothermally-grown gallium nitride crystal may be an n-type semiconductor, with a carrier concentration  $n$  between about  $10^{16}\text{ cm}^{-3}$  and  $10^{20}\text{ cm}^{-3}$  and a carrier mobility  $\eta$ , in units of centimeters squared per volt-second, such that the logarithm to the base 10 of  $\eta$  is greater than about  $-0.018557\text{ }n^3 + 1.0671\text{ }n^2 - 20.599\text{ }n + 135.49$ . The ammonothermally-grown gallium nitride crystal may be a p-type semiconductor, with a carrier concentration  $n$  between about  $10^{16}\text{ cm}^{-3}$  and  $10^{20}\text{ cm}^{-3}$  and a carrier mobility  $\eta$ , in units of centimeters squared per volt-second, such that the logarithm to the base 10 of  $\eta$  is greater than about  $-0.6546\text{ }n + 12.809$ .

By growing for a suitable period of time, the ammonothermally-grown crystalline group III metal nitride may have a thickness of greater than about 1 millimeter and a length, or diameter, greater than about 20 millimeters. In a preferred embodiment, the length is greater than about 50 millimeters or greater than about 100 millimeters. The crystalline group III nitride may be characterized by crystallographic radius of curvature of greater than 100 meters, greater than 1000 meter, or be greater than can be readily measured (infinite). After growth, the ammonothermally-grown crystalline group III metal nitride may be sliced, polished, and chemical-mechanically polished according to methods that are known in the art to form one or more wafers or crystalline substrate members. In a preferred embodiment, the root-mean-square surface roughness of the at least one wafer or crystalline substrate member is less than about one nanometer, for example, as measured by atomic force microscopy over an area of at least about 10 micrometers by 10 micrometers.

In another embodiment, the polycrystalline group III metal nitride is used as a source material for flux growth of at least one group III metal nitride single crystal, as described in U.S. Pat. No. 7,063,741 and in U.S. Patent Application 2006/0037529, each of which are hereby incorporated by reference in their entirety. The polycrystalline group III metal nitride and at least one flux are placed in a crucible and inserted into a furnace. The furnace is heated and the polycrystalline group III metal nitride is processed in a molten flux at a temperature greater than about 400 degrees Celsius and a pressure greater than about one atmosphere, during which at least a portion of the polycrystalline group III metal nitride is etched away and recrystallized onto at least one group III nitride crystal. Residual getter in the polycrystalline group III metal nitride is released into solution gradually, as the polycrystalline group III metal nitride is etched. Once in solution, the getter may react to form a getter metal nitride, amide, or halide. The getter may also be chemically bound to oxygen. The getter may remove residual oxygen in the molten flux, enabling growth of group III nitride single crystals with improved purity.

While the above is a full description of the specific embodiments, various modifications, alternative constructions and equivalents may be used. Therefore, the above description and illustrations should not be taken as limiting the scope of the present invention which is defined by the appended claims.

What is claimed is:

1. A polycrystalline gallium-containing group III metal nitride material, comprising:
  - a plurality of grains of a crystalline gallium-containing group III metal nitride;
    - the plurality of grains having an average grain size in a range of from about 10 nanometers to about 1 millimeter and defining a plurality of grain boundaries; and
    - the crystalline gallium-containing group III metal nitride having:
      - an atomic fraction of a gallium-containing group III metal in a range of from about 0.49 to about 0.55, the metal being selected from at least one of aluminum, indium, and gallium; and
      - an oxygen content in the form of a gallium-containing group III metal oxide or a substitutional impurity within the crystalline gallium-containing group III metal nitride less than about 10 parts per million (ppm); and
  - a plurality of inclusions within at least one of the plurality of grain boundaries and the plurality of grains, the plurality of inclusions comprising a getter, the getter constituting a distinct phase from the crystalline gallium-containing group III metal nitride and being incorporated into the polycrystalline gallium-containing group III metal nitride material at a level greater than about 200 parts per million.
2. The material as defined in claim 1, wherein the crystalline gallium-containing group III metal nitride has a porosity in volume fraction in a range of from about 0.1 percent to about 30 percent by volume; and an apparent density in a range of from about 70 percent to about 99.8 percent of a theoretical density value.
3. The material as defined in claim 1, wherein the getter comprises a metal.
4. The material as defined in claim 1, wherein the getter comprises at least one of alkaline earth metals, scandium, titanium, vanadium, chromium, yttrium, zirconium, niobium, the rare earth metals, hafnium, tantalum, tungsten, a nitride of any of the foregoing, and a halide of any of the foregoing.
5. The material as defined in claim 1, wherein the getter is present at a level greater than about 0.1% by weight.
6. The material as defined in claim 1, wherein the oxygen content present as a gallium-containing group III metal oxide or as a substitutional impurity within the crystalline gallium-containing group III metal nitride is less than about 3 parts per million (ppm).
7. The material as defined in claim 1, wherein the oxygen content present as a gallium-containing group III metal oxide or as a substitutional impurity within the crystalline gallium-containing group III metal is less than about 1 part per million (ppm).
8. The material as defined in claim 1, wherein the plurality of grains is characterized by a density from about 100 per cubic centimeter to about 10,000 per cubic centimeter.
9. The material as defined in claim 1, wherein the polycrystalline gallium-containing group III metal nitride material has a porosity from about 0.1 percent to about 10 percent by volume.

## 25

10. The material as defined in claim 1, wherein the polycrystalline gallium-containing group III metal nitride material has a porosity from about 10 percent to about 30 percent by volume.

11. The material as defined in claim 1, wherein each of the plurality of grains is characterized by an average grain diameter in a range of from about 1 millimeter to about 10 micrometers.

12. The material as defined in claim 1, wherein the plurality of grains is characterized by an average grain diameter greater than about 1.0 micrometer.

13. The material as defined in claim 1, wherein the polycrystalline gallium-containing group III metal nitride material is characterized by an apparent density in a range of from about 85 percent to about 95 percent of a theoretical value.

14. The material as defined in claim 1, wherein the atomic fraction of the gallium-containing group III metal in the polycrystalline gallium-containing group III metal nitride is in a range of from about 0.50 to about 0.51.

## 26

15. The material as defined in claim 1, wherein the polycrystalline gallium-containing group III metal nitride comprises one or more dopants to provide one or more of an n-type material, a p-type material, or a semi-insulating material.

16. The material as defined in claim 15, wherein the one or more of an n-type material, a p-type material, or a semi-insulating material is characterized by a dopant concentration in a range of from about  $10^{21}$  atoms per cubic centimeters to about  $10^{16}$  atoms per cubic centimeters.

17. The material as defined in claim 1, wherein the polycrystalline gallium-containing group III metal nitride material has an inter-grain bend strength greater than about 20 MegaPascal.

18. The material as defined in claim 1, wherein the plurality of inclusions comprise a material selected from a metal, a metal nitride, a metal halide, a metal oxynitride, a metal oxyhalide, a metal oxide, and a combination of any of the foregoing.

\* \* \* \* \*